Supporting Information

Iridium-catalyzed intramolecular enantioselective allylation of quinazolin-4(3*H*)-one derivatives

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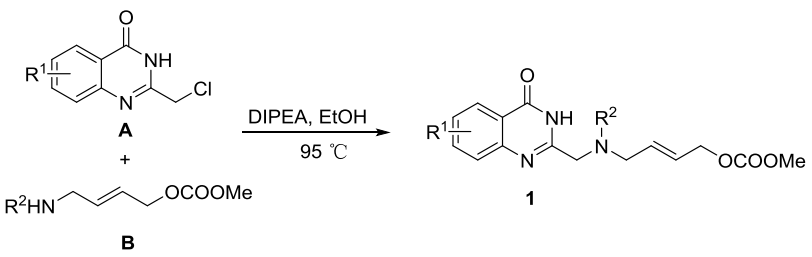
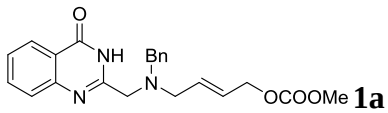
1. General Procedures

All reactions were carried out in dry solvents under a nitrogen atmosphere. (*E*)-4-(alkylamino)but-2-en-1-yl methyl carbonates[1] and the phosphoramidite ligands[2] were prepared according to the reported procedures. The reagents were purchased and used without further purification. The reactions were monitored by thin layer chromatography (TLC), and the products were isolated by silica gel column chromatography or preparative silica gel thin layer chromatography (*p*-TLC). Melting points were recorded on a Beijing Tech X-4 melting point apparatus. High-resolution mass spectra (HRMS) were recorded on LCMS-IT/TOF (SHIMADZU, Japan) with an electrospray ionization source. ^{1}H and ^{13}C NMR spectra were recorded on JOEL JNM-ECA 600 and JNM-ECS 400 using tetramethylsilane (TMS) as the internal standard. Chiral HPLC analysis was achieved using an Agilent 1100 Infinity series normal phase HPLC unit and Agilent Chemstation software. Daicel Chiralpak columns (250 × 4.6 mm) were used as specified in the text. Solvents were used of HPLC grade (Sigma Aldrich); all eluent systems were isocratic. Single crystal X-ray data were collected on a Bruker APEXII X-ray diffractometer equipped with a CMOS PHOTON 100 detector with a Cu Kα X-ray source (Kα = 1.54178 Å). Data were indexed, integrated and scaled using DENZO and SCALEPACK from the HKL program suite (Otwinowski & Minor, 1997). Structure of (*R*)-**2b** was solved through direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-2014) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. The data obtained were deposited at the Cambridge Crystallographic Data Centre.

2. Synthesis and Characterization of 1a-1w



To a solution of **B** (3.0 mmol) and *N*,*N*-diisopropylethylamine (DIPEA) (3.0 mmol) in EtOH (5.0 mL) was added **A**[3] (2.0 mmol) at room temperature. The mixture was stirried at 95 °C overnight.[4] After the reaction completed (monitored by TLC), the crude reaction mixture was cooled to room temperature and filtered. The residue was collected, and recrystallized from hot ethanol to give **1**.



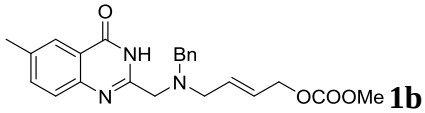
1a

(*E*)-4-(Benzyl((4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1a)

Creamy-white solid. 597 mg, 76% yield, m.p.= 103-104 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.84 (br, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.50 - 7.46 (m, 1H), 7.37 (d, J = 7.3 Hz, 2H), 7.31 - 7.27 (m, 2H), 7.22 - 7.19 (m, 1H), 5.98-5.91 (m, 1H), 5.76-5.69 (m, 1H), 4.54 (d, J = 6.0 Hz, 2H), 3.69 (s, 2H), 3.67 (s, 3H), 3.17 (d, J = 6.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.7, 155.4, 154.2, 148.8, 137.0, 134.5, 131.0, 129.1, 128.5, 128.3, 127.6, 126.9, 126.5, 126.4, 121.6, 67.3, 58.8, 56.2, 55.9, 54.7.



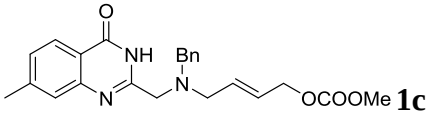
1b

(*E*)-4-(Benzyl((6-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1b)

White solid. 643 mg, 79% yield, m.p.= 112-113 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.75 (br, 1H), 7.88 (s, 1H), 7.62 - 7.59 (m, 1H), 7.53 (d, J = 8.2 Hz, 1H), 7.38 - 7.36 (m, 2H), 7.31 - 7.27 (m, 2H), 7.23 - 7.19 (m, 1H), 5.94 (dt, J = 15.6 Hz, 6.4, 1H), 5.72 (dt, J = 15.6 Hz, 6.0, 1H), 4.54 (d, J = 5.5 Hz, 2H), 3.68 (s, 5H), 3.57 (s, 2H), 3.16 (d, J = 6.4 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.6, 155.5, 153.2, 146.8, 137.1, 136.9, 136.1, 130.9, 129.2, 128.7, 128.5, 127.8, 126.8, 126.0, 121.4, 67.4, 59.0, 56.1, 56.0, 54.9, 21.3.



1c

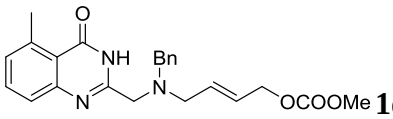
(*E*)-4-(Benzyl((7-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-

en-1-yl methyl carbonate (1c)

Light yellow solid. 610 mg, 75% yield, m.p.= 101-102 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (br, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 5.93 (dt, *J* = 15.6 Hz, 6.4, 1H), 5.72 (dt, *J* = 15.6 Hz, 6.0, 1H), 4.54 (d, *J* = 6.0 Hz, 2H), 3.69 (s, 2H), 3.68 (s, 3H), 3.57 (s, 2H), 3.17 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5, 155.6, 154.1, 149.1, 145.8, 137.1, 130.9, 129.3, 128.8, 128.6, 128.3, 127.9, 126.9, 126.5, 119.3, 67.5, 59.1, 56.2, 56.1, 55.0, 22.0.



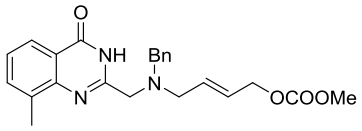
1d

(*E*)-4-(Benzyl((5-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1d)

White solid. 578 mg, 71% yield, m.p.= 101-102 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.60 (br, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.32 - 7.28 (m, 2H), 7.24 - 7.20 (m, 2H), 5.97 - 5.90 (m, 1H), 5.76 - 5.69 (m, 1H), 4.54 (d, *J* = 5.5 Hz, 2H), 3.68-3.67 (m, 5H), 3.55 (s, 2H), 3.33 (s, 3H), 3.16 (d, *J* = 6.0 Hz, 2H), 2.76 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.2, 155.6, 153.7, 150.5, 141.4, 137.1, 133.8, 130.9, 129.3, 129.2, 128.8, 128.6, 127.9, 125.2, 120.2, 67.5, 59.0, 56.1, 55.9, 55.0, 23.0.



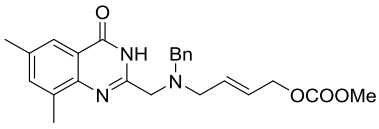
1e

(*E*)-4-(Benzyl((8-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1e)

White solid. 545 mg, 67% yield, m.p.= 113-114 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (br, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.39 - 7.34 (m, 3H), 7.31 - 7.28 (m, 2H), 7.23 - 7.19 (m, 1H), 5.93 (dt, *J* = 15.6 Hz, 6.4, 1H), 5.75 (dt, *J* = 15.6 Hz, 6.0, 1H), 4.55 (d, *J* = 6.0 Hz, 2H), 3.75 (s, 2H), 3.68 (s, 3H), 3.62 (s, 2H), 3.23 (d, *J* = 6.0 Hz, 2H), 2.54 (s, 3H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 162.2, 155.5, 152.6, 147.6, 137.2, 135.6, 135.3, 131.1, 129.3, 128.7, 128.4, 127.8, 126.1, 124.2, 121.6, 67.5, 58.8, 56.3, 55.9, 54.9, 17.7.



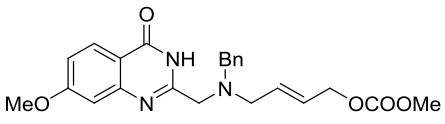
1f

(*E*)-4-(Benzyl((6,8-dimethyl-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1f)

White solid. 615 mg, 73% yield, m.p.= 126-127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (br, 1H), 7.90 (s, 1H), 7.40 (s, 1H), 7.35 - 7.32 (m, 4H), 7.27 - 7.26 (m, 1H), 5.94 - 5.87 (m, 1H), 5.83 - 5.77 (m, 1H), 4.61 (d, *J* = 5.5 Hz, 2H), 3.78 (s, 3H), 3.68 (s, 2H), 3.64 (s, 2H), 3.20 (d, *J* = 6.4 Hz, 2H), 2.54 (s, 3H), 2.42 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.2, 155.6, 151.2, 145.6, 137.2, 136.8, 136.2, 135.4, 131.2, 129.3, 128.7, 128.4, 127.8, 123.7, 121.4, 67.6, 58.9, 56.3, 55.9, 54.9, 21.3, 17.6.



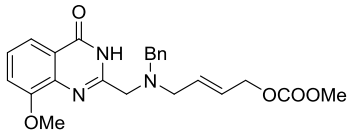
1g

(*E*)-4-(Benzyl((7-methoxy-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1g)

White solid. 550 mg, 65% yield, m.p.= 123-124 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (br, 1H), 7.98 (dd, *J* = 8.7 Hz, 1.8 Hz, 1H), 7.38-7.36 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.20 (m, 1H), 7.08-7.04 (m, 2H), 5.97-5.91 (m, 1H), 5.76-5.70 (m, 1H), 4.54 (d, *J* = 6.0 Hz, 2H), 3.88 (s, 3H), 3.69-3.68 (m, 5H), 3.57 (s, 2H), 3.17 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.8, 161.2, 155.5, 154.9, 151.1, 137.0, 131.0, 129.2, 128.6, 128.4, 128.0, 127.7, 116.5, 115.0, 108.9, 67.4, 58.9, 56.2, 56.0, 55.6, 54.8.



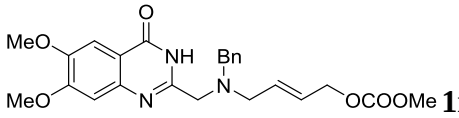
1h

(*E*)-4-(Benzyl((8-methoxy-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1h)

White solid. 584 mg, 69% yield, m.p.= 146-147 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (br, 1H), 7.63 (dd, J = 7.8 Hz, 0.9 Hz, 1H), 7.42-7.38 (m, 3H), 7.33-7.27 (m, 3H), 7.22-7.19 (m, 1H), 5.98-5.91 (m, 1H), 5.77-5.70 (m, 1H), 4.54 (d, J = 6.0 Hz, 2H), 3.90 (s, 3H), 3.68 (s, 3H), 3.66 (s, 2H), 3.59 (s, 2H), 3.15 (d, J = 6.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 155.6, 154.2, 153.5, 139.4, 137.1, 130.9, 129.2, 128.8, 128.6, 127.9, 126.9, 122.9, 118.0, 114.5, 67.4, 59.0, 56.3, 56.2, 56.1, 54.9.



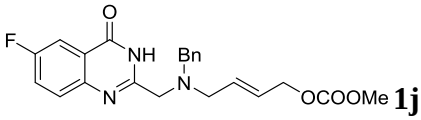
1i

(*E*)-4-(Benzyl((6,7-dimethoxy-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino) but-2-en-1-yl methyl carbonate (1i)

White solid. 643 mg, 71% yield, m.p.= 134-135 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (br, 1H), 7.57 (s, 1H), 7.36-7.32 (m, 4H), 7.28-7.26 (m, 1H), 7.04 (s, 1H), 5.93-5.86 (m, 1H), 5.83-5.77 (m, 1H), 4.60 (d, J = 5.5 Hz, 2H), 3.98 (s, 3H), 3.97 (s, 3H), 3.77 (s, 3H), 3.67 (s, 2H), 3.61 (s, 2H), 3.20 (d, J = 6.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.0, 155.6, 155.2, 152.8, 149.0, 145.2, 137.1, 131.0, 129.3, 128.8, 128.6, 127.9, 114.9, 107.7, 105.6, 67.5, 59.1, 56.4, 56.3, 56.1, 54.9.



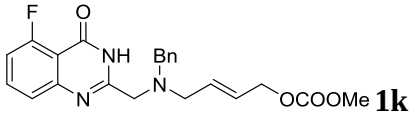
1j

(*E*)-4-(Benzyl((6-fluoro-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1j)

Light yellow solid. 556 mg, 63% yield, m.p.= 124-125 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.99 (br, 1H), 7.75-7.64 (m, 3H), 7.37-7.35 (m, 2H), 7.29-7.26 (m, 2H), 7.21-7.17 (m, 1H), 5.95-5.89 (m, 1H), 5.74-5.68 (m, 1H), 4.53 (d, J = 5.5 Hz, 2H), 3.68-3.67 (m, 5H), 3.58 (s, 2H), 3.17 (d, J = 5.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.0 (d, J_{FC} = 2.9 Hz), 160.7 (d, J_{FC} = 248.2 Hz), 155.5, 153.5, 145.5, 137.0, 130.9, 129.3 (d, J_{FC} = 8.6 Hz), 129.2, 128.6, 128.5, 127.7, 123.1, 122.8 (d, J_{FC} = 9.6 Hz), 111.4 (d, J_{FC} = 24.0 Hz), 67.4, 59.0, 56.1, 54.8.



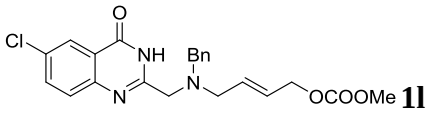
1k

(*E*)-4-(Benzyl((5-fluoro-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1k)

Brown solid. 630 mg, 77% yield, m.p.= 114-115 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (br, 1H), 7.67-7.62 (m, 1H), 7.41-7.39 (m, 1H), 7.32-7.26 (m, 5H), 7.11-7.06 (m, 1H), 5.94-5.87 (m, 1H), 5.84-5.77 (m, 1H), 4.60 (d, *J* = 5.0 Hz, 2H), 3.77 (s, 3H), 3.69 (s, 2H)， 3.61 (s, 2H), 3.23 (d, *J* = 5.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.8 (d, J_{FC} = 232.3 Hz), 160.0, 158.9, 155.4 (d, J_{FC} = 13.8 Hz), 150.9, 136.9, 134.9(d, J_{FC} = 10.5 Hz), 130.9, 129.2, 128.6, 128.5, 127.7, 122.9 (d, J_{FC} = 3.8 Hz), 113.1 (d, J_{FC} = 21.1 Hz), 111.3 (d, J_{FC} = 6.7 Hz), 67.4, 59.0, 56.2, 55.9, 54.8.



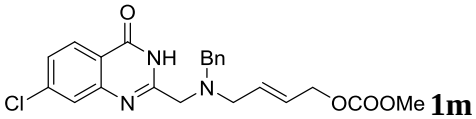
1l

(*E*)-4-(Benzyl((6-chloro-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1l)

Light yellow solid. 642 mg, 75% yield, m.p.= 116-117 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.0 (br, 1H), 8.00 (d, *J* = 2.3 Hz, 1H), 7.81 (dd, *J* = 8.7 Hz, 2.8 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.37-7.35 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.18 (m, 1H), 5.93 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.72 (dt, *J* = 15.6 Hz, 6.0 Hz, 1H), 4.53 (d, *J* = 6.0 Hz, 2H), 3.69-3.67 (m, 5H), 3.59 (s, 2H), 3.17 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 160.6, 155.7, 155.0, 147.1, 138.2, 134.4, 131.8, 130.6, 129.2, 129.0, 128.1, 127.1, 127.0, 124.8, 122.6, 67.3, 57.3, 56.4, 54.7, 54.6.



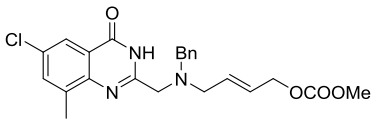
1m

(*E*)-4-(Benzyl((7-chloro-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1m)

White solid. 608 mg, 71% yield, m.p.= 118-119 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (br, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.51 (dd, *J* = 8.7 Hz, 1.8Hz, 1H),7.37 - 7.35 (m, 2H), 7.30 - 7.26 (m, 2H), 7.21 - 7.18 (m, 1H), 5.93 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.73 (dt, *J* = 15.6 Hz, 6.0 Hz, 1H), 4.53 (d, *J* = 6.0 Hz, 2H), 3.69 (s, 2H), 3.67 (s, 3H), 3.59 (s, 2H), 3.17 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 155.6, 155.5, 149.9, 140.9, 136.9, 130.8, 129.3, 128.8, 128.7, 128.0, 127.9, 127.3, 126.7, 120.2, 67.4, 59.3, 56.4, 56.1, 55.0.



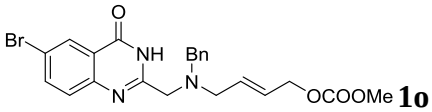
1n

(*E*)-4-(Benzyl((6-chloro-8-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)methyl) amino)but-2-en-1-yl methyl carbonate (1n)

White solid. 681 mg, 77% yield, m.p.= 117-118 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (br, 1H), 8.05 (d, *J* = 2.3 Hz, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.35 - 7.30 (m, 4H), 7.28 - 7.26 (m, 1H), 5.90 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.80 (dt, *J* = 15.6 Hz, 6.0 Hz, 1H), 4.61 (d, *J* = 5.5 Hz, 2H), 3.77 (s, 3H), 3.68 (s, 2H), 3.64 (s, 2H), 3.22 (d, *J* = 6.4 Hz, 2H), 2.54 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 155.6, 153.0, 146.2, 138.0, 137.1, 135.3, 131.7, 130.9, 129.3, 128.8, 128.6, 127.9, 123.5, 122.7, 67.5, 59.1, 56.2, 56.1, 54.9, 17.5.



1o

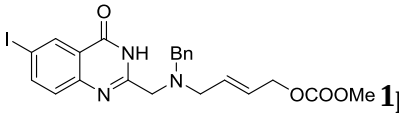
(*E*)-4-(Benzyl((6-bromo-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1o)

Pale yellow solid. 642 mg, 68% yield, m.p.= 113-114 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.05 (br, 1H), 8.16 (d, *J* = 2.8 Hz, 1H), 7.93 (dd, *J* = 8.9 Hz, 2.8 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.29 - 7.27

(m, 2H), 7.21 - 7.19 (m, 1H), 5.95-5.91 (m, 1H), 5.75-5.71 (m, 1H), 4.53 (d, *J* = 5.5 Hz, 2H), 3.69 - 3.68 (m, 5H), 3.59 (s, 2H), 3.18 (d, *J* = 6.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 155.5, 154.7, 147.7, 137.8, 136.9, 130.7, 129.3, 129.1, 128.9, 128.8, 128.7, 127.9, 123.1, 120.2, 67.4, 59.2, 56.4, 56.1, 54.9.



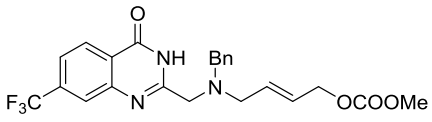
1p

(*E*)-4-(Benzyl((6-iodo-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1p)

Pale yellow solid. 747 mg, 72% yield, m.p.= 91-92 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.01 (br, 1H), 8.34 (d, *J* = 1.8 Hz, 1H), 8.06 (dd, *J* = 8.7 Hz, 1.8 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.37 - 7.35 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.18 (m, 1H), 5.92 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.72 (dt, *J* = 15.6 Hz, 6.0 Hz, 1H), 4.53 (d, *J* = 6.0 Hz, 2H), 3.68 - 3.67 (m., 5H), 3.57 (s, 2H), 3.17 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 155.5, 154.9, 148.2, 143.4, 136.9, 135.4, 130.7, 129.3, 128.9, 128.7, 128.6, 127.9, 123.3, 91.0, 67.4, 59.2, 56.3, 56.2, 54.9.



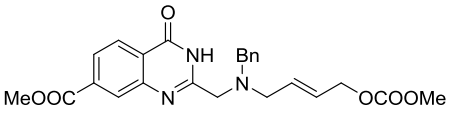
1q

(*E*)-4-(Benzyl((4-oxo-7-(trifluoromethyl)-3,4-dihydroquinazolin-2-yl)methyl) amino)but-2-en-1-yl methyl carbonate (1q)

Khaki solid. 645 mg, 70% yield, m.p.= 77-78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (br, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.35 - 7.28 (m, 4H), 7.25 - 7.21 (m, 1H), 5.95 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.83 (dt, *J* = 15.6 Hz, 6.0 Hz, 1H), 4.60 (d, *J* = 6.0 Hz, 2H), 3.75 (s, 3H), 3.72 (s, 2H), 3.68 (s, 2H), 3.26 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 155.8, 155.6, 148.9, 136.9, 136.1 (q, *J* = 32.6 Hz), 130.8, 129.9, 129.3, 128.8, 127.9, 127.7, 124.6 (q, *J* = 3.8 Hz), 124.1, 122.7 (q, *J* = 2.9 Hz), 123.4 (q, *J* = 273.2 Hz), 67.4, 59.3, 56.5, 56.1, 54.9.



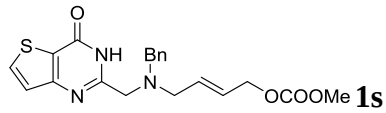
1r

Methyl(*E*)-2-((benzyl(4-((methoxycarbonyl)oxy)but-2-en-1-yl)amino)methyl)-4-oxo-3,4-dihydroquinazoline-7-carboxylate (1r)

White solid. 667 mg, 74% yield, m.p. = 115-116 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (br, 1H), 8.30-8.28 (m, 2H), 8.05 (dd, *J* = 8.2 Hz, 1.4Hz, 1H), 7.32-7.29 (m, 4H), 7.25 - 7.22 (m, 1H), 5.90 (dt, *J* = 15.6 Hz, 6.4Hz, 1H), 5.81 (dt, *J* = 15.6 Hz, 6.0Hz, 1H), 4.60 (d, *J* = 5.5 Hz, 2H), 3.96 (s, 3H), 3.76 (s, 3H), 3.70 (s, 2H), 3.65(s, 2H), 3.24 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 161.0, 155.6, 155.0, 148.9, 136.9, 135.8, 130.7, 129.4, 129.0, 128.9, 128.9, 128.0, 127.0, 126.8, 124.8, 67.4, 59.3, 56.5, 56.1, 55.0, 52.8.



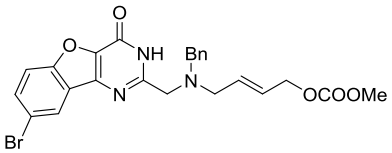
1s

(*E*)-4-(Benzyl((4-oxo-3,4-dihydrothieno[3,2-d]pyrimidin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1s)

White solid. 535 mg, 67% yield, m.p.= 125-126 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (br, 1H), 7.74 (d, *J* = 5.5 Hz,1H), 7.30 - 7.27 (m, 4H), 7.24 - 7.18 (m, 2H), 5.92-5.85 (m, 1H), 5.80-5.73 (m, 1H), 4.56 (d, *J* = 5.2 Hz, 2H), 3.72 (s, 3H), 3.64 (s, 2H), 3.62 (s, 2H), 3.18 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 157.8, 156.2, 155.6, 136.9, 134.5, 130.8, 129.3, 128.8, 128.6, 127.9, 124.9, 122.3, 67.5, 59.1, 56.2, 55.8, 54.9.



1t

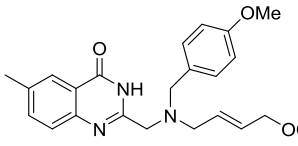
(*E*)-4-(Benzyl((8-bromo-4-oxo-3,4-dihydrobenzofuro[3,2-d]pyrimidin-2-yl) methyl)amino)but-2-en-1-yl methyl carbonate (1t)

White solid. 554 mg, 54% yield, m.p.= 156-157 ºC.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.57 (br, 1H), 8.19 (s, 1H), 7.89 (s, 2H), 7.38 (d, *J* = 6.9 Hz, 2H), 7.30-7.26 (m, 2H), 7.21 - 7.18 (m, 1H), 5.92 (dt, *J* = 15.6 Hz, 6.4Hz,

1H), 5.75 (dt, *J* = 15.6 Hz, 6.0Hz, 1H), 4.54 (d, *J* = 6.0 Hz, 2H), 3.72 (s, 2H), 3.69 (s, 2H), 3.66 (s, 3H), 3.20 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 157.7, 155.5, 155.4, 153.5, 142.6, 139.6, 138.8, 132.8, 132.3, 129.5, 128.6, 127.6, 127.5, 125.0, 124.1, 117.0, 115.7, 67.8, 57.8, 56.5, 55.1.



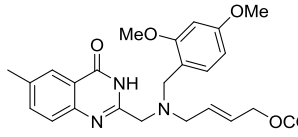
1u

(*E*)-4-((4-Methoxybenzyl)((6-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)methyl) amino)but-2-en-1-yl methyl carbonate (1u)

White solid. 567 mg, 67% yield, m.p.= 141-142 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.72 (br, 1H), 7.88 (s, 1H), 7.60 (dd, *J* = 8.2 Hz, 1.8 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 5.93 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.72 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 4.54 (d, *J* = 6.0 Hz, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 3.60 (s, 2H), 3.54 (s, 2H), 3.13 (d, *J* = 6.4Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 159.2, 155.5, 153.3, 146.9, 136.8, 136.1, 131.0, 130.5, 129.0, 128.4, 126.8, 126.0, 121.4, 114.1, 67.5, 58.3, 56.0, 55.9, 55.3, 54.9, 21.3.



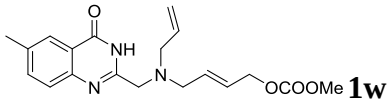
1v

(*E*)-4-((2,4-Dimethoxybenzyl)((6-methyl-4-oxo-3,4-dihydroquinazolin-2-yl) methyl)amino)but-2-en-1-yl methyl carbonate (1v)

Yellow solid. 588 mg, 63% yield, m.p.= 96-97 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.21 (br, 1H), 7.89 (s, 1H), 7.61-7.59 (m, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 1H), 6.45 (dd, *J* = 8.2 Hz, 2.8 Hz, 1H), 5.90 (dt, *J* = 15.6 Hz, 6.4 Hz, 1H), 5.73 (dt, *J* = 15.6 Hz, 6.0 Hz, 1H), 4.54 (d, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.57 (s, 2H), 3.56 (s, 2H), 3.14 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 161.0, 159.4, 155.6, 154.3, 147.2, 136.4, 135.9, 132.5, 131.6, 127.9, 126.6, 126.0, 121.5, 117.4, 103.9, 98.9, 67.6, 56.1, 55.7, 55.4, 55.2, 55.0, 54.8, 21.3.



1w

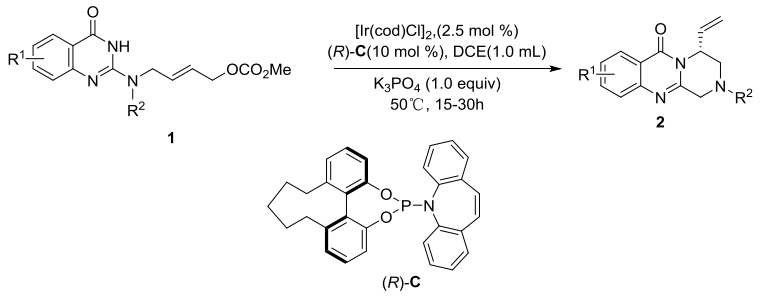
(*E*)-4-(Allyl((6-methyl-4-oxo-3,4-dihydroquinazolin-2-yl)methyl)amino)but-2-en-1-yl methyl carbonate (1w)

White solid. 364 mg, 51% yield, m.p.= 95-96 °C.

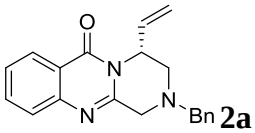
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.68 (br, 1H), 7.89 (s, 1H), 7.62-7.59 (m, 1H), 7.52 (d, J = 8.2 Hz, 1H), 5.93-5.84 (m, 2H), 5.77-5.70 (m, 1H), 5.20-5.11 (m, 2H), 4.54 (d, J = 5.5 Hz, 2H), 3.67 (s, 3H), 3.52 (s, 2H), 3.20-3.16 (m, 4H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) 161.7, 155.6, 153.4, 147.1, 136.9, 136.2, 133.8, 130.9, 128.4, 126.9, 126.1, 121.5, 119.8, 67.5, 57.6, 56.1, 55.9, 54.9, 21.3.

3. Synthesis and Characterization of 2a-2u



In a sealed tube, $[Ir(cod)Cl]_2$ and (*R*)-**C** were dissolved in anhydrous 1,2-dichloroethane (DCE) with nitrogen atmosphere and vigorously stirred for 15 min, and a light red solution appeared. **1** and K_3PO_4 were added to the solution, and the resulting mixture was stirred at 50 °C until **1** was consumed completely (monitored by TLC). The reaction mixture was filtered through a celite pad, and the filtrate was concentrated in vacuo. The residue was purified by *prep*-TLC to give **2** (eluent: EtOAc/ petroleum ether = 1/2), and the enantiomeric excess was determined by chiral HPLC analysis.



2a

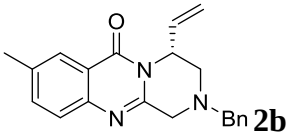
(*R*)-2-Benzyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2a)

Pale yellow solid. m.p. = 146-147 °C, 24.5 mg, 77% yield, 93% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 16.9 min, t (major) = 21.2 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.2 Hz, 1H), 7.73-7.69 (m, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.44-7.40 (m, 1H), 7.35-7.28 (m, 5H), 6.05 (ddd, *J* = 16.9 Hz, 10.1 Hz, 6.9 Hz, 1H), 5.29-5.21 (m, 3H), 4.07 (d, *J* = 16.9 Hz, 1H), 3.73-3.64 (m, 2H), 3.44 (d, *J* = 16.9 Hz, 1H), 3.14 (d, *J* = 11.9 Hz, 1H), 2.71 (dd, *J* = 11.9 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.4, 151.6, 147.4, 136.7, 135.8, 134.5, 129.1, 128.6, 127.8, 127.0 ,126.6, 126.5, 120.9, 117.9, 62.0, 57.0, 54.8, 54.6.

ESI-MS: $[M+H]^+$ m/z 318.2



2b

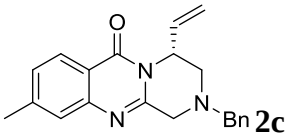
(*R*)-2-Benzyl-8-methyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2b)

Light yellow solid. m.p. = 125-126 °C, 26.8 mg, 81% yield, 98% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 23.1 min, t (major) = 43.4 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.52 (dd, *J* = 8.2 Hz, 2.3 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.36-7.27 (m, 5H), 6.03 (ddd, *J* = 16.9 Hz, 10.1 Hz, 6.4 Hz, 1H), 5.25-5.19 (m, 3H), 4.05 (dd, *J* = 16.8 Hz, 1.8 Hz, 1H), 3.71-3.63 (m, 2H), 3.42 (d, *J* = 16.9 Hz, 1H), 3.12 (d, *J* = 12.4 Hz, 1H), 2.70 (dd, *J* = 12.4 Hz, 4.1 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 150.7, 145.3, 136.7, 136.5, 136.0, 135.8, 129.1, 128.6, 127.7, 126.4, 126.3, 120.6, 117.7, 62.0, 57.0, 54.7, 54.5, 21.4.

ESI-MS: $[M+H]^+$ m/z 332.1



2c

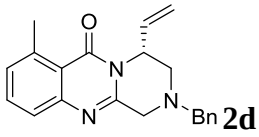
(*R*)-2-Benzyl-9-methyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2c)

Light yellow solid. m.p. = 110-111 ºC, 27.0 mg, 82% yield, 97% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 17.3 min, t (major) = 20.2 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.34-7.28 (m, 6H), 7.23 (d, *J* = 8.2 Hz, 1H), 6.08-5.99 (m, 1H), 5.25-5.19 (m, 3H), 4.06 (d, *J* = 16.9 Hz, 1H), 3.73-3.62 (m, 2H), 3.42 (d, *J* = 16.9 Hz, 1H), 3.14-3.10 (m, 1H), 2.70-2.67 (m, 1H), 2.46 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 151.6, 147.5, 145.5, 136.7, 135.9, 129.1, 128.6, 128.1, 127.7, 126.8, 126.3, 118.5, 117.7, 62.0, 57.0, 54.7, 54.4, 22.0.

ESI-MS: $[M+H]^+$ m/z 332.1



2d

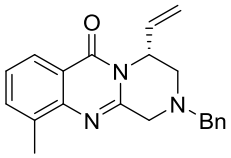
(*R*)-2-Benzyl-7-methyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (7e)

Colourless oil. 25.2 mg, 76% yield, 93% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 85/15, ν = 1.0 mL/min, λ = 220 nm, t (major) = 12.7 min, t (minor) = 15.8 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 1H), 7.40-7.26 (m, 6H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.08-5.99 (m, 1H), 5.26-5.18 (m, 3H), 4.04 (d, *J* = 16.5 Hz, 1H), 3.73-3.63 (m, 2H), 3.41 (d, *J* = 16.0 Hz, 1H), 3.13 (dd, *J* = 12.4 Hz, 1.8 Hz, 1H), 2.86 (s, 3H), 2.69-2.66 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 151.4, 148.9, 141.4, 136.8, 136.3, 133.6, 129.1, 129.1, 128.6, 127.8, 124.8, 119.5, 117.4, 62.0, 56.9, 55.0, 54.2, 23.2.

ESI-MS: $[M+H]^+$ m/z 332.1



2e

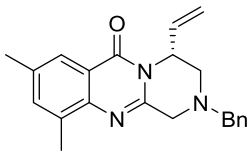
(*R*)-2-Benzyl-10-methyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2e)

Colourless oil. 26.1 mg, 79% yield, 98% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 95/5, ν = 1.0 mL/min, λ = 220 nm, t (major) = 18.5 min, t (minor) = 22.9 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.39-7.28 (m, 6H), 6.04 (ddd, *J* = 16.9 Hz, 10.1 Hz, 6.4 Hz, 1H), 5.26-5.19 (m, 3H), 4.15-4.10 (m, 1H), 3.76-3.62 (m, 2H), 3.46 (d, *J* = 16.9 Hz, 1H), 3.12 (dt, *J* = 12.4 Hz, 1.8 Hz, 1H), 2.72-2.67 (m, 1H), 2.54 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 150.2, 146.1, 136.9, 135.9, 135.2, 134.9, 129.0, 128.6, 127.7, 125.9, 124.6, 120.8, 117.6, 62.0, 57.3, 54.7, 54.5, 17.4.

ESI-MS: $[M+H]^+$ m/z 332.1



2f

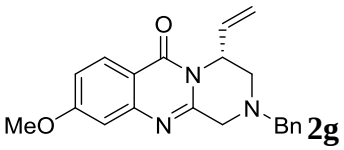
(*R*)-2-Benzyl-8,10-dimethyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2f)

Colourless oil. 28.0 mg, 81% yield, 94% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 85/15, ν = 1.0 mL/min, λ = 220 nm, t (major) = 10.9 min, t (minor) = 12.9 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.38-7.33 (m, 6H), 6.03 (ddd, *J* = 16.9 Hz, 10.5 Hz, 6.9 Hz, 1H), 5.24-5.17 (m, 3H), 4.10 (dd, *J* = 16.5 Hz, 1.8 Hz, 1H), 3.75-3.61 (m, 2H), 3.44 (d, *J* = 16.5 Hz, 1H), 3.12 (dt, *J* = 11.9 Hz, 1.8 Hz, 1H), 2.69 (dd, *J* = 11.9 Hz, 3.7 Hz,1H), 2.51 (s, 3H), 2.41 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 149.3, 144.1, 137.0, 136.6, 136.0, 135.9, 134.9, 129.0, 128.6, 127.7, 124.0, 120.7, 117.5, 62.0, 57.3, 54.8, 54.4, 21.4, 17.3.

ESI-MS: $[M+H]^+$ m/z 346.1



2g

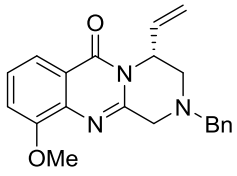
(*R*)-2-Benzyl-9-methoxy-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2g)

Colourless oil. 27.4 mg, 79% yield, 97% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 25.0 min, t (major) = 26.6 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz,1H), 7.35-7.28 (m, 5H), 6.99 (dd, *J* = 9.2 Hz, 2.3 Hz, 1H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.04 (ddd, *J* = 16.9 Hz, 10.1 Hz, 6.9 Hz, 1H), 5.29-5.19 (m, 3H), 4.04 (d, *J* = 16.5 Hz, 1H), 3.87 (s, 3H), 3.72-3.63 (m, 2H), 3.42 (d, *J* = 16.9 Hz, 1H), 3.13 (d, *J* = 12.4 Hz, 1H), 2.69 (dd, *J* = 12.4 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.8, 160.9, 152.4, 149.6, 136.7, 136.0, 129.1, 128.6, 128.5, 127.8, 117.7, 116.7, 114.4, 107.0, 62.0, 56.9, 55.7, 54.8, 54.4.

ESI-MS: $[M+H]^+$ m/z 348.1



2h

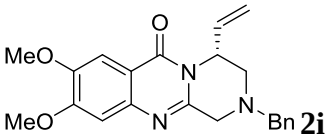
(*R*)-2-Benzyl-10-methoxy-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazoli-n-6-one (2h)

Colourless oil. 28.1 mg, 81% yield, 97% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (major) = 29.8 min, t (minor) = 58.3 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz,1H), 7.37-7.27 (m, 6H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.04 (ddd, *J* = 17.4 Hz, 10.5 Hz, 6.9 Hz, 1H), 5.26-5.20 (m, 3H), 4.17 (d, *J* = 16.9 Hz, 1H), 3.98 (s, 3H), 3.71-3.62 (m, 2H), 3.45 (d, *J* = 16.9 Hz, 1H), 3.14 (d, *J* = 12.4 Hz, 1H), 2.73 (dd, *J* = 11.9 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ161.2, 154.0, 151.2, 138.1, 136.8, 135.8, 129.2, 128.6, 127.8, 126.7, 122.0, 118.3, 117.9, 114.0, 62.1, 57.3, 56.3, 55.0, 54.7.

ESI-MS: $[M+H]^+$ m/z 348.1



2i

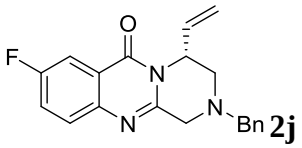
(*R*)-2-Benzyl-8,9-dimethoxy-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-b]quinaz-olin-6-one (2i)

Colourless oil. 29.5 mg, 78% yield, 95% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 61.4 min, t (major) = 82.9 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.34-7.27 (m, 5H), 6.95 (s, 1H), 6.04 (ddd, *J* = 16.9 Hz, 10.5 Hz, 6.9 Hz, 1H), 5.28-5.19 (m, 3H), 4.02 (d, *J* = 16.5 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.71-3.62 (m, 2H), 3.41 (d, *J* = 16.5 Hz, 1H), 3.12 (d, *J* = 11.9 Hz, 1H), 2.69 (dd, *J* = 11.9 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 155.2, 150.3, 148.9, 143.6, 136.7, 136.0, 129.1, 128.6, 127.7, 117.7, 114.1, 106.9, 105.8, 62.0, 56.8, 56.3, 54.8, 54.5.

ESI-MS: $[M+H]^+$ m/z 378.2



2j

(*R*)-2-Benzyl-8-fluoro-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2j)

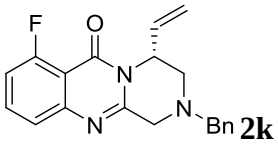
Light yellow oil. 26.1 mg, 78% yield, 95% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 0.8 mL/min, λ = 220 nm, t (minor) =14.7 min, t (major) = 19.5 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 7.57-7.53 (m, 1H), 7.444-7.39 (m, 1H), 7.34-7.27 (m, 5H), 6.03 (ddd, *J* = 16.9 Hz, 10.5 Hz, 6.9 Hz, 1H), 5.28-5.18 (m, 3H), 4.05 (d, *J* = 16.9 Hz, 1H), 3.72-3.63 (m, 2H), 3.42 (d, *J* = 16.9 Hz, 1H), 3.13 (d, *J* = 12.4 Hz, 1H), 2.70 (dd, *J* = 11.9 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7 (d, J_{FC} = 3.8 Hz), 160.6 (d, J_{FC} = 247.3 Hz), 150.9, 144.0, 136.6, 135.6, 129.1, 129.0 (d, J_{FC} = 8.3 Hz), 128.6, 127.8, 123.2 (d, J_{FC}

= 24.9 Hz), 122.0 (d, J_{FC} = 8.6 Hz), 118.1, 111.7 (d, J_{FC} = 23.0 Hz), 62.0, 56.9, 54.8, 54.7.

ESI-MS: $[M+H]^+$ m/z 336.1



2k

(*R*)-2-Benzyl-7-fluoro-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2k)

Light yellow solid. m.p. = 141-142 °C. Prepared by following the general procedure with (*R*)-**C** as the ligand. 24.3 mg, 72% yield, 88% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 16.3 min, t (major) = 17.3 min].

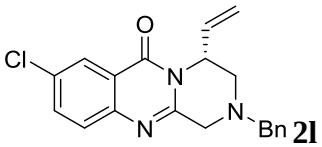
Prepared by following the general procedure with (*R*)-**B** as the ligand. 21.8 mg, 65% yield, 76% *ee*.

Prepared by following the general procedure with (*R*)-**D** as the ligand. 24.8 mg, 74% yield, 89% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.59 (m, 1H), 7.35-7.27 (m, 6H), 7.07-7.02 (m, 1H), 6.08-5.99 (m, 1H), 5.31-5.25 (m, 2H), 5.20-5.18 (m, 1H), 4.04 (dd, *J* = 16.9, 1.8 Hz, 1H), 3.71-3.64 (m, 2H), 3.41 (d, *J* = 16.9 Hz, 1H), 3.13 (dt, *J* = 12.4, 1.8 Hz, 1H), 2.69 (dd, *J* = 12.4 Hz, 4.1 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.4 (d, J_{FC} = 265.5 Hz), 158.3 (d, J_{FC} = 3.8 Hz), 152.8, 149.4, 136.6, 135.4, 134.8 (d, J_{FC} = 10.5 Hz), 129.1, 128.6, 127.8, 122.5(d, J_{FC} = 4.8 Hz), 118.5, 112.9 (d, J_{FC} = 21.1 Hz), 110.7 (d, J_{FC} = 5.8 Hz), 62.0, 56.8, 54.8, 54.4.

ESI-MS: $[M+H]^+$ m/z 336.1



2l

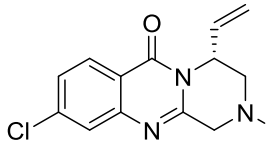
(*R*)-2-Benzyl-8-chloro-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2l)

Light yellow oil. 28.2 mg, 80% yield, 93% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 0.8 mL/min, λ = 220 nm, t (minor) = 18.1 min, t (major) = 31.2 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.49 (d, *J* = 8.7Hz 1H), 7.35-7.27 (m, 5H), 5.90 (ddd, *J* = 16.9 Hz, 10.1 Hz, 6.9 Hz, 1H), 5.27-5.19 (m, 3H), 4.05 (d, *J* = 16.9 Hz, 1H), 3.72-3.64 (m, 2H), 3.42 (d, *J* = 16.9 Hz, 1H), 3.13 (t, *J* = 11.9 Hz, 1H), 2.70 (dd, *J* = 12.4 Hz, 3.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 151.9, 145.9, 136.6, 135.5, 134.9, 132.1, 129.1, 128.6, 128.3, 127.8, 126.3, 121.9, 118.1, 62.0, 56.9, 54.8, 54.6.

ESI-MS: $[M+H]^+$ m/z 352.1



2m

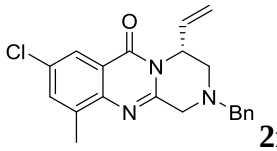
(*R*)-2-Benzyl-9-chloro-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2m)

Light yellow oil. 29.1 mg, 82% yield, 90% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 11.6 min, t (major) = 13.6 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.37-7.29 (m, 6H), 6.03 (ddd, *J* = 17.4 Hz, 10.5 Hz, 6.9 Hz, 1H), 5.27-5.16 (m, 3H), 4.06 (dd, *J* = 16.9 Hz, 1.8 Hz, 1H), 3.73-3.63 (m, 2H), 3.43 (d, *J* = 16.9 Hz, 1H), 3.12 (dt, *J* = 11.9 Hz, 1.8 Hz, 1H), 2.70 (dd, *J* = 12.4 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 153.0, 148.3, 140.7, 136.6, 135.6, 129.1, 128.6, 128.4, 127.8, 127.1, 126.2, 119.3, 118.1, 61.9, 56.9, 54.7 54.6.

ESI-MS: $[M+H]^+$ m/z 352.1



2n

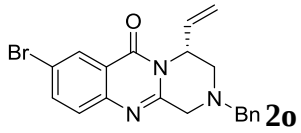
(*R*)-2-Benzyl-8-chloro-10-methyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2n)

Pale yellow solid. m.p. = 134-135 ^{o}C. 27.1 mg, 74% yield, 92% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol =75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 7.7 min, t (major) = 8.6 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.49 (s, 1H), 7.37-7.31 (m, 5H), 6.03 (ddd, *J* = 17.4 Hz, 10.5 Hz, 6.9 Hz, 1H), 5.29-5.19 (m, 3H), 4.10 (d, *J* = 16.9 Hz, 1H), 3.75-3.62 (m, 2H), 3.44 (d, *J* = 16.9 Hz, 1H), 3.12 (d, *J* = 11.9 Hz, 1H), 2.70 (dd, *J* = 12.4 Hz, 3.7 Hz, 1H), 2.51 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7, 150.5, 144.7, 137.6, 136.8, 135.6, 135.0, 131.4, 129.0, 128.6, 127.8, 123.7, 121.8, 117.9, 62.0, 57.3, 54.7, 54.6, 17.3.

ESI-MS: $[M+H]^+$ m/z 366.1



2o

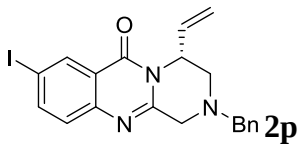
(*R*)-2-Benzyl-8-bromo-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2o)

Light yellow oil. 29.3 mg, 74% yield, 89% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 16.4 min, t (major) = 31.5 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.3 Hz, 1H), 7.77 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.35-7.27 (m, 5H), 6.02 (ddd, *J* = 16.9 Hz, 10.1 Hz, 6.9 Hz, 1H), 5.27-5.19 (m, 3H), 4.04 (d, *J* = 16.9 Hz, 1H), 3.72-3.64 (m, 2H), 3.41 (d, *J* = 16.9 Hz, 1H), 3.13 (d, *J* = 12.4 Hz, 1H), 2.71 (dd, *J* = 11.9 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.2, 152.1, 146.2, 137.7, 136.6, 135.5, 129.5, 129.1, 128.6, 128.5, 127.8, 122.2, 119.8, 118.2, 62.0, 57.0, 54.8, 54.6.

ESI-MS: $[M+H]^+$ m/z 397.1



2p

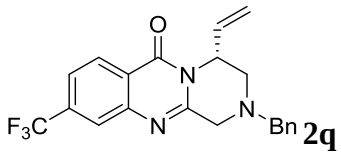
(*R*)-2-Benzyl-8-iodo-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2p)

Yellow oil. 31.0 mg, 70% yield, 90% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 17.8 min, t (major) = 38.4 min].

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.3 Hz, 1H), 7.95 (dd, *J* = 8.7 Hz, 1.8 Hz, 1H), 7.35-7.28 (m, 6H), 6.02 (ddd, *J* = 16.9 Hz, 10.0 Hz, 6.9 Hz, 1H), 5.27-5.21 (m, 3H), 4.05 (dd, *J* = 16.9 Hz, 1.8 Hz, 1H), 3.73-3.64 (m, 2H), 3.41 (d, *J* = 16.9 Hz, 1H), 3.13 (d, *J* = 11.9 Hz, 1H), 2.71 (dd, *J* = 12.4 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 152.3, 146.6, 143.2, 136.6, 135.8, 135.5, 129.1, 128.6, 128.5, 127.8, 122.5, 118.2, 90.6, 62.0, 57.0, 54.8, 54.6.

ESI-MS: $[M+H]^+$ m/z 444.1



2q

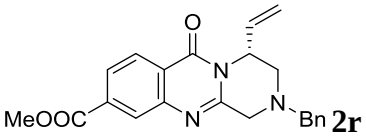
(*R*)-2-Benzyl-9-(trifluoromethyl)-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*] quinazolin-6-one (2q)

Colourless oil. 26.6mg, 78% yield, 84% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 0.7 mL/min, λ = 220 nm, t (minor) = 9.9 min, t (major) = 11.0 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 2.3 Hz, 1H), 7.78 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.35-7.28 (m, 5H), 6.03 (ddd, *J* = 16.9 Hz, 10.1 Hz, 6.9 Hz, 1H), 5.27-5.19 (m, 3H), 4.05 (dd, *J* = 16.9 Hz, 1.4 Hz, 1H), 3.73-3.64 (m, 1H), 3.42 (d, *J* = 16.9 Hz, 1H), 3.14 (t, *J* = 11.9 Hz, 1H), 2.71 (dd, *J* = 12.4 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.6, 153.2, 147.3, 136.5, 136.0 (q, *J* = 32.6 Hz), 135.4, 129.1, 128.7, 128.1, 127.9, 124.3 (q, *J* = 3.8 Hz), 123.5 (q, *J* = 273.2 Hz), 123.1, 122.4 (q, *J* = 2.9 Hz), 118.3, 61.9, 57.0, 55.0, 54.6.

ESI-MS: $[M+H]^+$ m/z 386.1



2r

Methyl-(*R*)-2-benzyl-6-oxo-4-vinyl-1,3,4,6-tetrahydro-2*H*-pyrazino[2,1-*b*]quinazo -line-9-carboxylate (2r)

Pale yellow oil. Prepared by following the general procedure with (*R*)-**C** as the ligand. 26.6mg, 71% yield, 82% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 24.0 min, t (major) = 38.8 min].

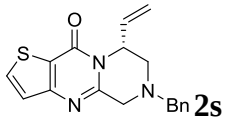
Prepared by following the general procedure with (*R*)-**B** as the ligand. 25.5 mg, 68% yield, 83% *ee*.

Prepared by following the general procedure with (*R*)-**D** as the ligand. 25.1 mg, 67% yield, 85% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.25 (m, 2H), 8.02 (dd, *J* = 8.2 Hz, 1.4Hz, 1H), 7.36-7.29 (m, 5H), 6.04 (ddd, *J* = 16.9 Hz, 10.5 Hz, 6.9Hz, 1H), 5.28-5.20 (m, 3H), 4.10 (dd, *J* = 16.5 Hz, 1.8Hz, 1H), 3.96 (s, 3H), 3.75-3.64 (m, 2H), 3.46 (d, *J* = 16.9 Hz, 1H), 3.14 (d, *J* = 12.4 Hz, 1H), 2.73-2.69 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 160.9, 152.5, 147.2, 136.6, 135.6, 135.5, 129.1, 128.7, 128.6, 127.9, 127.3, 126.4, 123.8, 118.2, 62.0, 57.0, 54.9, 54.7, 52.7.

ESI-MS: $[M+H]^+$ m/z 376.1



2s

(*R*)-6-Benzyl-8-vinyl-5,6,7,8-tetrahydro-10*H*-pyrazino[1,2-*a*]thieno[3,2-*d*]pyrimid-in-10-one (2s)

Colourless oil. Prepared by following the general procedure with (*R*)-**C** as the ligand. 22.3 mg, 69% yield, 86% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 16.1 min, t (major) = 22.0 min].

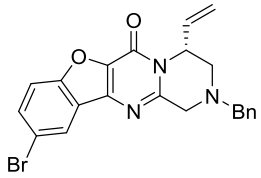
Prepared by following the general procedure with (*R*)-**B** as the ligand. 20.3 mg, 63% yield, 70% *ee*.

Prepared by following the general procedure with (*R*)-**D** as the ligand. 22.0 mg, 68% yield, 94% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 5.0 Hz, 1H), 7.35-7.28 (m, 5H), 7.20 (d, *J* = 5.5 Hz, 1H), 6.04 (ddd, *J* = 17.4 Hz, 10.5 Hz, 6.9 Hz, 1H), 5.27-5.21 (m, 3H), 4.10 (dd, *J* = 16.9 Hz, 1.8 Hz, 1H), 3.74-3.64 (m, 2H), 3.45 (d, *J* = 16.9 Hz, 1H), 3.15 (d, *J* = 11.9 Hz, 1H), 2.69 (dd, *J* = 11.9 Hz, 3.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.6, 156.2, 153.2, 136.6, 135.6, 134.6, 129.1, 128.6, 127.8, 124.6, 121.5, 118.2, 61.9, 56.8, 54.5.

ESI-MS: $[M+H]^+$ m/z 324.1



2t

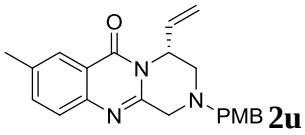
(*R*)-2-Benzyl-10-bromo-4-vinyl-1,2,3,4-tetrahydro-6*H*-benzofuro[3,2-*d*]pyrazino [1,2-*a*]pyrimidin-6-one (2t)

Colurless oil. 33.1 mg, 76% yield, 85% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 85/15, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 31.3 min, t (major) = 35.0 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.66-7.63 (m, 1H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.36-7.30 (m, 5H), 6.05 (ddd, *J* = 16.9 Hz, 10.5 Hz, 6.9 Hz, 1H), 5.33-5.22 (m, 3H), 4.20 (d, *J* = 17.4 Hz, 1H), 3.77-3.66 (m, 2H), 3.51 (d, *J* = 17.4 Hz, 1H), 3.18 (d, *J* = 12.4 Hz, 1H), 2.71 (dd, *J* = 12.4 Hz, 3.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.8, 153.5, 152.8, 141.6, 138.3, 136.5, 135.3, 132.7, 129.1, 128.7, 127.9, 124.4, 124.3, 118.5, 117.2, 114.6, 61.8, 56.9, 54.9, 54.1.

ESI-MS: $[M+H]^+$ m/z 437.1



2u

(*R*)-2-(4-Methoxybenzyl)-8-methyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*] quinazolin-6-one (2u)

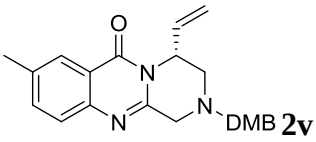
Pale yellow solid. m.p = 126-127 °C. 29.3 mg, 80% yield, 96% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 28.9 min, t (major) = 34.1 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.07-5.99 (m, 1H), 5.25-5.20 (m, 3H), 4.05 (d, *J* = 16.5 Hz, 1H), 3.82 (s, 3H), 3.68-3.58 (m, 2H), 5.10-5.05 (m, 1H), 4.70 (d, *J* = 14.8 Hz, 1H), 4.55 (d, *J* = 14.8 Hz, 1H), 3.90 (s, 3H),

3.41 (d, *J* = 16.9 Hz, 1H), 3.13 (d, *J* = 11.9 Hz, 1H), 2.68 (dd, *J* = 12.4, 3.7 Hz, 1H), 2.47 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.4, 159.2, 150.8, 145.3, 136.5, 136.0, 135.9, 130.3, 128.7, 126.4, 126.3, 120.6, 117.7, 114.0, 61.4, 56.9, 55.4, 54.6, 54.5, 21.4.

ESI-MS: $[M+H]^+$ m/z 362.1



2v

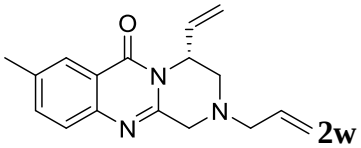
(*R*)-2-(3,4-Dimethylbenzyl)-8-methyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino [2,1-*b*]quinazolin-6-one (2v)

Colourless oil. 30.2 mg, 79% yield, 97% *ee* [Daicel Chiralpak OD-H, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 15.5 min, t (major) = 19.9 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.52 (dd, *J* = 8.2 Hz, 1.8 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.25-7.22 (m, 1H), 6.48-6.45 (m, 2H), 6.03 (ddd, *J* = 16.7 Hz, 10.5 Hz, 6.9Hz, 1H), 5.25-5.19 (m, 3H), 4.04 (dd, *J* = 16.9, 1.8 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.68 (s, 2H), 3.46 (d, *J* = 16.5 Hz, 1H), 3.15 (dt, *J* = 12.4, 1.8 Hz, 1H), 2.71 (dd, *J* = 11.9 Hz, 3.7 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5, 160.5, 159.0, 151.2, 145.4, 136.4, 136.1, 136.0, 131.6, 126.3, 120.6, 117.6, 116.9, 104.3, 98.6, 56.6, 55.5, 54.8, 54.7, 54.6, 21.4.

ESI-MS: $[M+H]^+$ m/z 392.2



2w

(*R*)-2-Allyl-8-methyl-4-vinyl-1,2,3,4-tetrahydro-6*H*-pyrazino[2,1-*b*]quinazolin-6-one (2w)

White solid. 21.5 mg, 76% yield, 96% *ee* [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (major) = 13.8 min, t (minor) = 18.5 min].

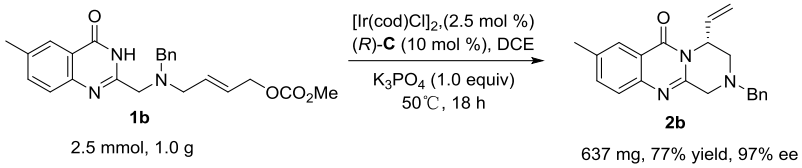
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.55-7.47 (m, 2H), 6.05-5.96 (m, 1H),, 5.90-5.80 (m, 1H), 5.30-5.20 (m, 5H), 4.08 (d, *J* = 16.0 Hz, 1H), 3.39 (d, *J* = 16.5 Hz,

1H), 3.22-3.15 (m, 2H), 3.11-3.06 (m, 1H), 2.63 (dd, *J* = 11.9 Hz, 3.7 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.4, 150.7, 145.4, 136.6, 136.0, 135.9, 133.7, 126.4, 126.3, 120.6, 119.2, 117.7, 60.6, 57.1, 54.7, 54.5, 21.4.

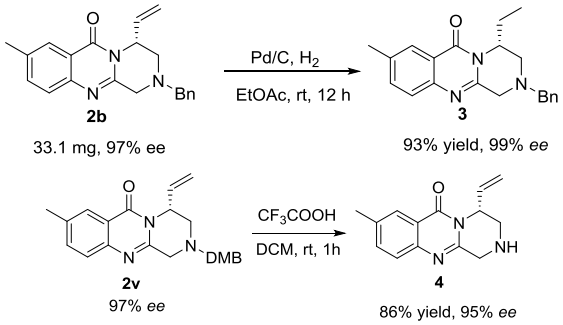
ESI-MS: $[M+H]^+$ m/z 282.2

4. Scale Synthesis of 2b



$[Ir(cod)Cl]_2$ (51 mg, 2.5 mol%) and (*R*)-**C** (143 mg, 10 mol%) were placed in a 50 mL three neck flask fitted with a rubber septum and a nitrogen balloon, and then the mixture was degassed and backfilled with nitrogen for three cycles. DCE (15 mL) was added by syringe, and the mixture was stirred at room temperature for 15 min. **1b** (2.5 mmol, 1.0 g) and K_3PO_4 (2.5 mmol, 530 mg, 1.0 equiv) was added to the tube. The mixture was stirred at 50 ^oC for 18 h. The resulting solution was concentrated and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 2:1) to give product **2b**. Yield: 637 mg (77%), 97% ee. Light yellow solid.

5. Application of the Synthesized 2b and 2v



2b (0.1 mmol), palladium on activated carbon (5% Pd) (6.0 mg) and EtOAc (3.0 mL) were added to a round bottom flask fitted with a hydrogen balloon. The tube was degassed and backfilled with hydrogen for three cycles. The mixture was stirred until

TLC showed that the reaction completed. The reaction mixture was filtered through a celite pad, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4/1) to give product **3**.

CF_3COOH (0.5 mL) was added to a solution of CH_2Cl_2 (DCM) (2.0 mL) containing **2v** (30.2 mg, 0.084 mmol), and then stirred at room temperature until the material was consumed completely (monitored by TLC). $NaHCO_3$ (1 M) was added to neutralize the acid. The product was extracted with DCM (3 × 5 mL), and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (DCM/MeOH = 20:1) to afford the desired product **4**.

3: Light yellow solid, m.p. = 117-118 ºC. 31.1 mg, 93% yield, 99% ee [Daicel Chiralpak ID-H, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 220 nm, t (minor) =13.1 min, t (major) = 26.0 min];

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.38-7.26 (m, 5H), 4.49 (d, *J* = 10.1 Hz, 1H), 4.06 (d, *J* = 16.9 Hz, 1H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.58 (d, *J* = 12.8 Hz, 1H), 3.40 (d, *J* = 16.5 Hz, 1H), 3.14 (d, *J* = 12.4 Hz, 1H), 2.45-2.40 (m, 4H), 1.98-1.92 (m, 1H), 1.82-1.76 (m, 1H), 0.85 (t, *J* = 7.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5, 151.0, 145.4, 137.1, 136.4, 135.9, 129.2, 128.6, 127.7, 126.3, 126.1, 120.6, 62.1, 57.4, 54.5, 51.0, 25.3, 21.4, 10.8.

ESI-MS: $[M+H]^+$ m/z 334.2

4: Light yellow solid. m.p. = 123-124 ºC. 16.2 mg, 86% yield, 95% ee [Daicel Chiralpak OD-H, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 220 nm, t (minor) = 11.5 min, t (major) = 13.7 min];

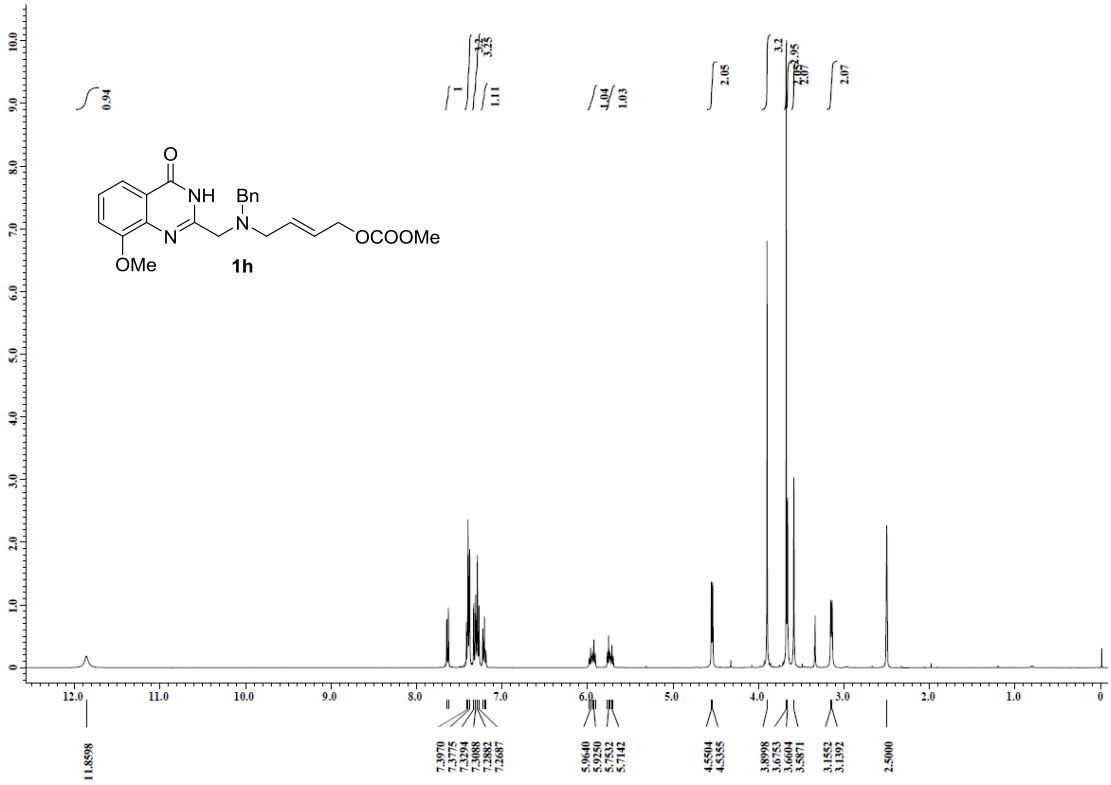
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.55-7.48 (m, 2H), 6.01-5.92 (m, 1H), 5.30-5.27 (m, 2H), 4.86 (d, *J* = 17.4 Hz, 1H), 4.15-4.01 (m, 2H), 3.31-3.21 (m, 2H), 2.45 (s, 3H), 1.94 (br, 1H);

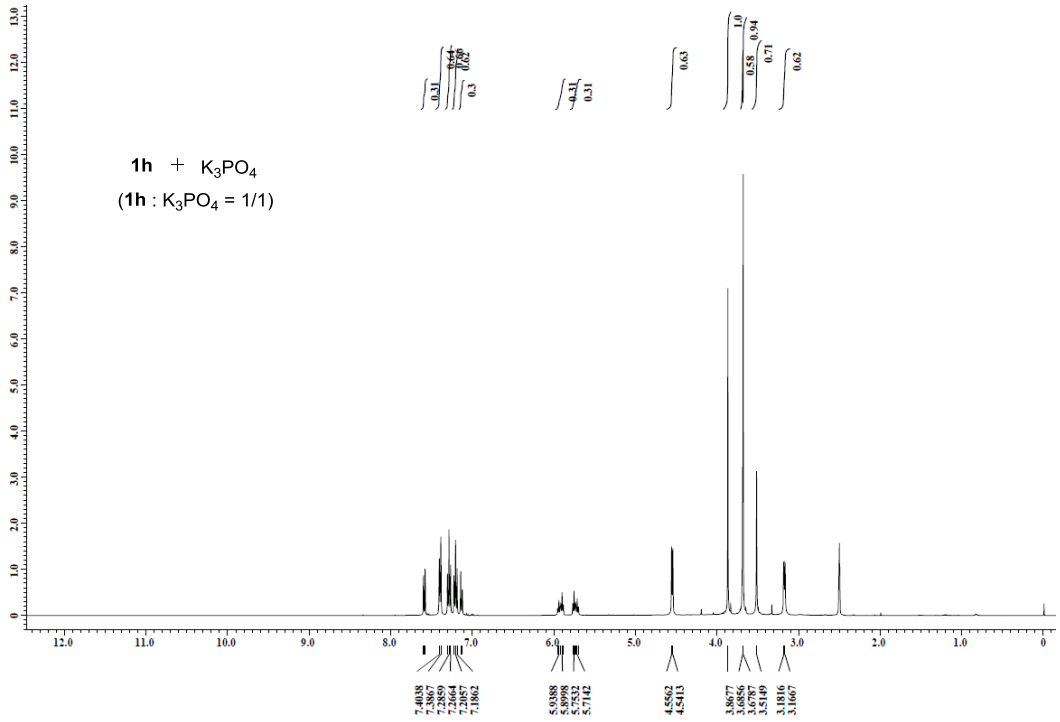
^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3, 151.5, 145.1, 136.6, 136.2, 135.4, 126.4, 126.4, 120.4, 117.1, 52.2, 49.2, 46.8, 21.4.

ESI-MS: $[M+H]^+$ m/z 242.2

6. Expermient of mixing K_3PO_4 with substrate 1h

K_3PO_4 (0.1 mmol, 21.2 mg) was added to a solution of DMSO-d_6 (0.5 mL) containing **1h** (42.3 mg, 0.1 mmol), the mixture was stirred at room temperature about 2 minutes, then tested its ^{1}H-NMR spectrum immediately.





7. X-Ray Crystallographic Data for (*R*)-2b (CCDC 1898661)

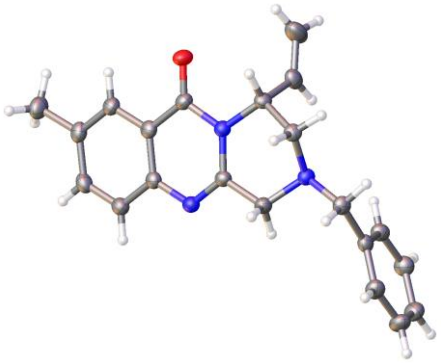


Table 1: Crystal Data and Structure Refinement for CCDC 1898661.

Identification code	CCDC 1898661
Empirical formula	$C_{21}H_{21}N_3O$
Formula weight	331.41
Temperature/K	173.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.1516(2)
b/Å	5.26734(13)
c/Å	17.9860(4)
α/°	90
β/°	94.683(2)
γ/°	90
Volume/Å^3	864.11(3)
Z	2
ρ_{calc}g/cm^3	1.274
μ/mm^{-1}	0.631
F(000)	352.0
Crystal size/mm^3	0.4 × 0.08 × 0.05

Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.696 to 143.028
Index ranges	$-11 \leq h \leq 10$, $-5 \leq k \leq 6$, $-21 \leq l \leq 22$
Reflections collected	12553
Independent reflections	3145 [R_{int} = 0.0460, R_{sigma} = 0.0378]
Data/restraints/parameters	3145/1/235
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0911
Final R indexes [all data]	R_1 = 0.0395, wR_2 = 0.0936
Largest diff. peak/hole / e $Å^{-3}$	0.14/-0.17
Flack parameter	-0.1(2)

8. **References**

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2 (*a*) J. Y. Hamilton, D. Sarlah and E. M. Carreira, *Org. Synth.*, 2015, **92**, 1; (*b*) P. Zhang, J. Yu, F. Peng, X. Wu, J. Jie, C. Liu, H. Tian, H. Yang and H. Fu, *Chem. Eur. J*., 2016, **22**, 17477.

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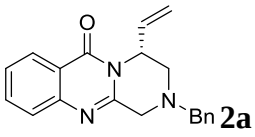
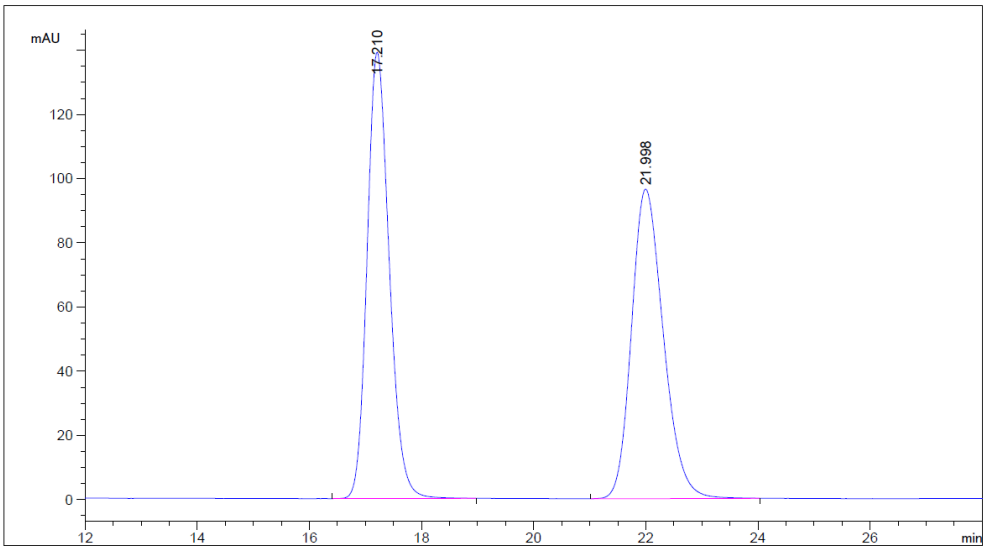
9. HPLC analysis of products 2a-2w and 3-4



2a



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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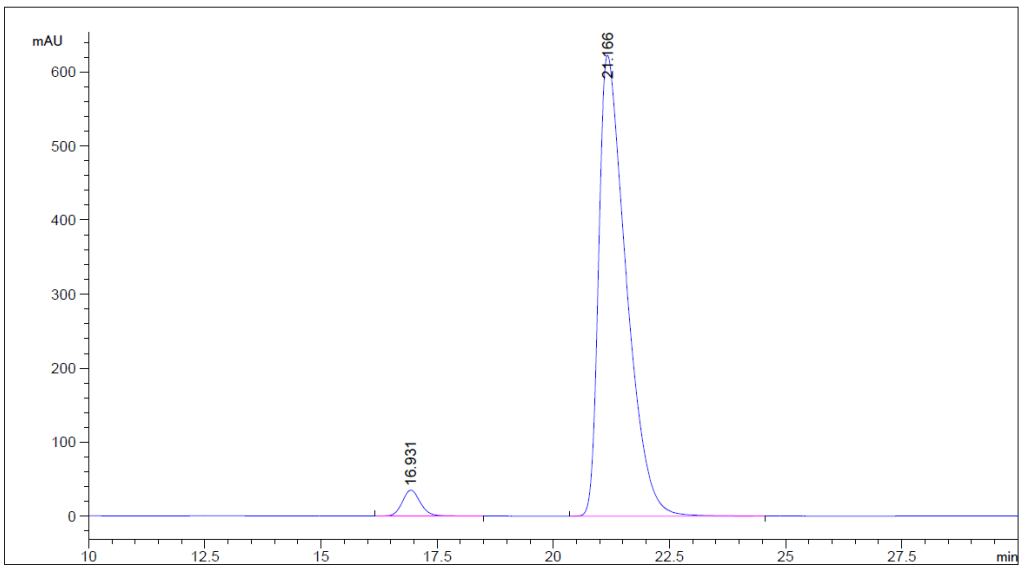
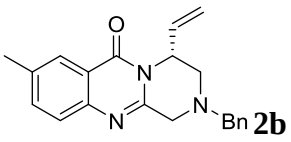
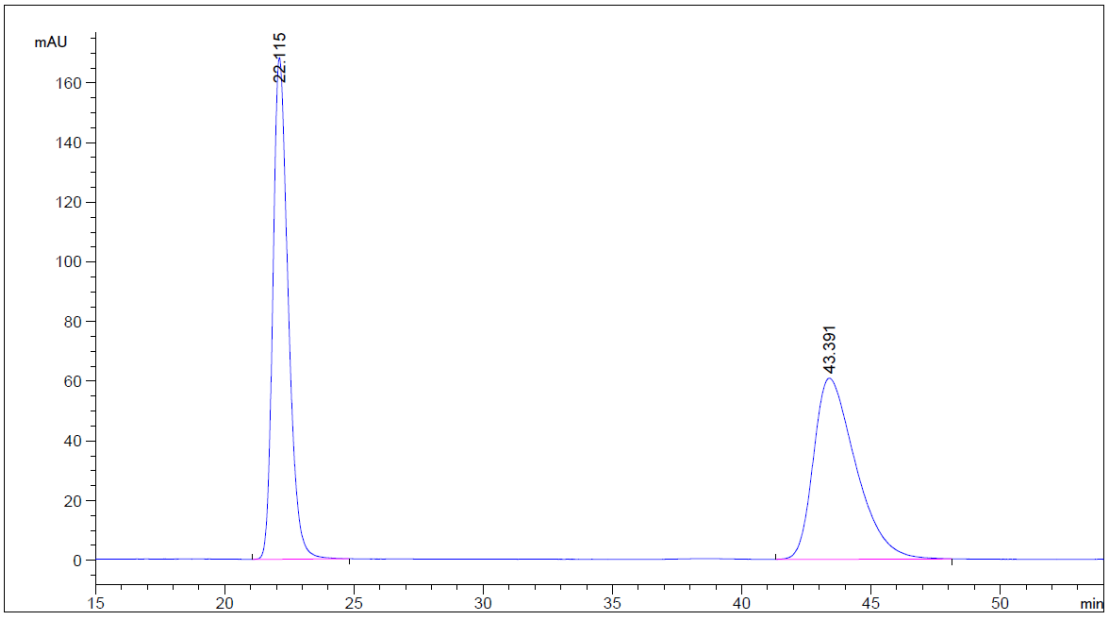
2	21.998	BB	0.6084	3802.06812	96.45722	49.9343



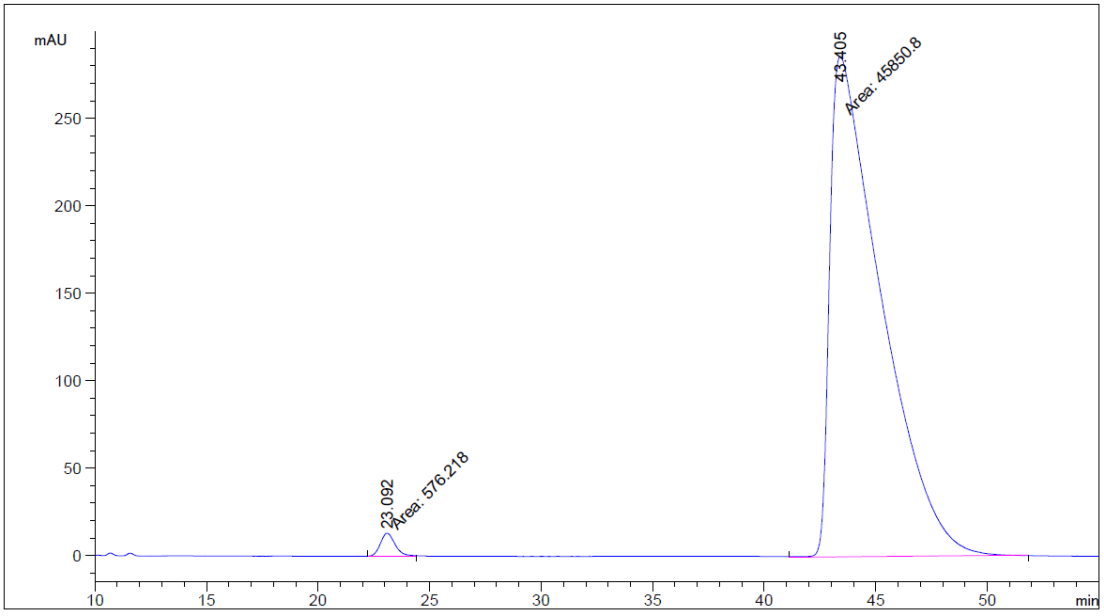
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.931	BB	0.4161	945.95209	34.96712	3.5729
2	21.166	BB	0.6140	2.55301e4	622.29047	96.4271



2b



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.115	BB	0.6287	6897.43555	168.10358	50.0978
2	43.391	BB	1.6042	6870.49609	60.64320	49.9022



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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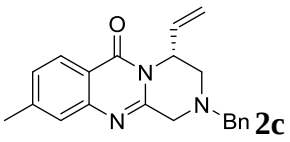
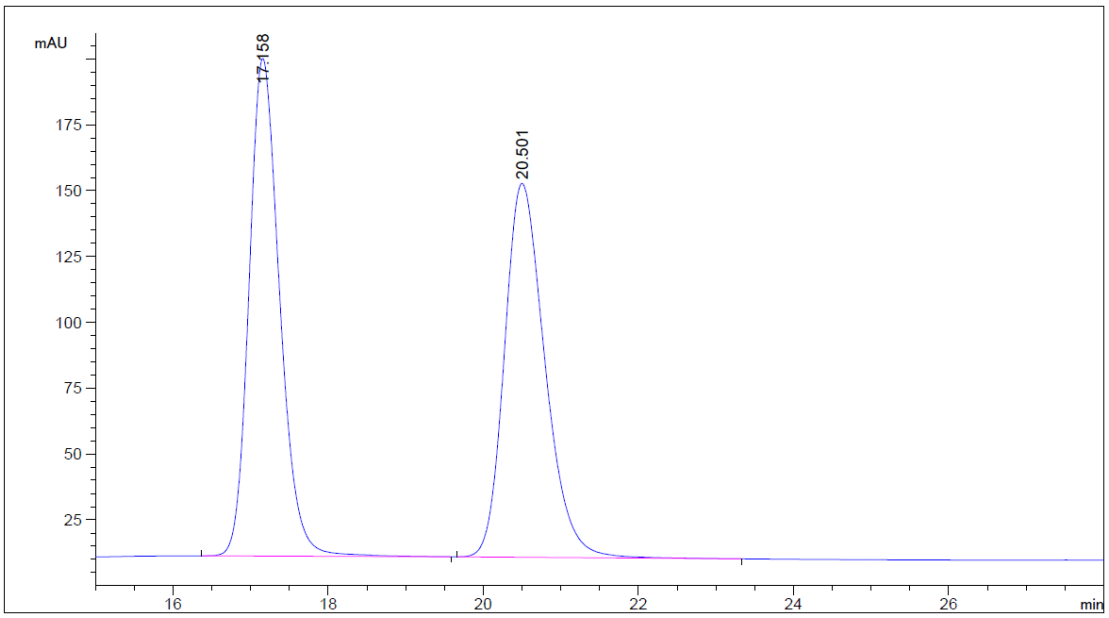


2c



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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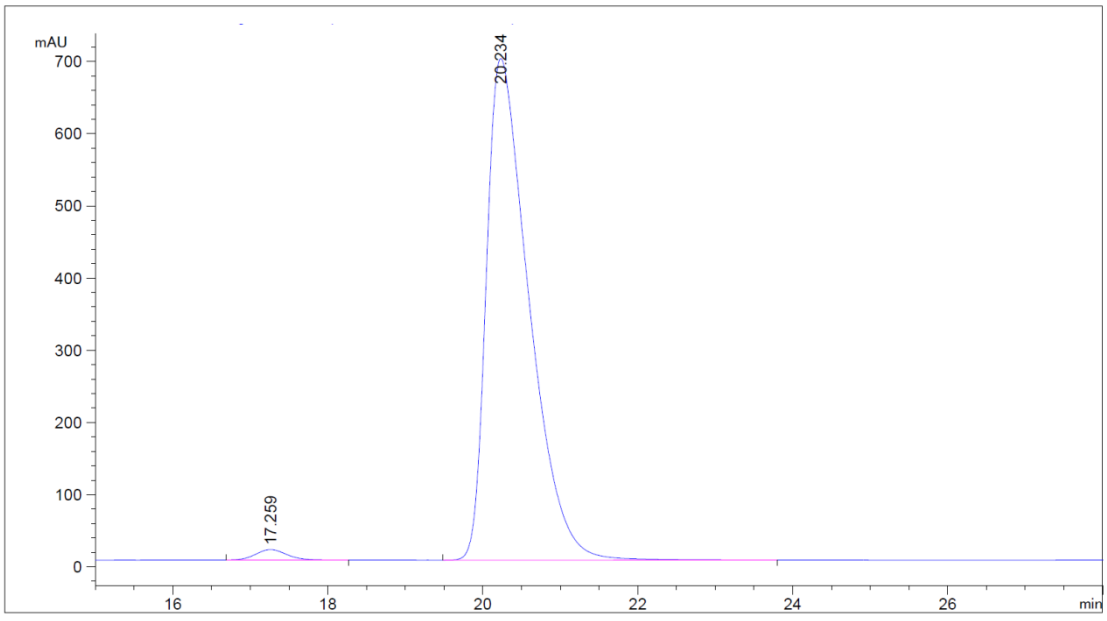
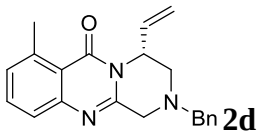
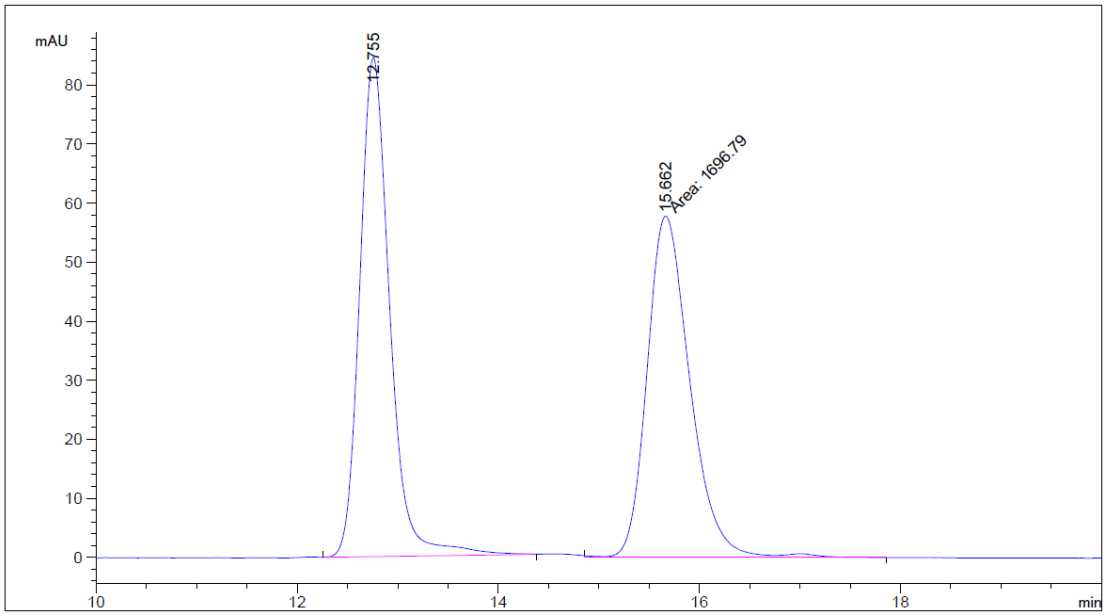
2	20.501	BB	0.5582	5145.35693	141.97826	49.8606



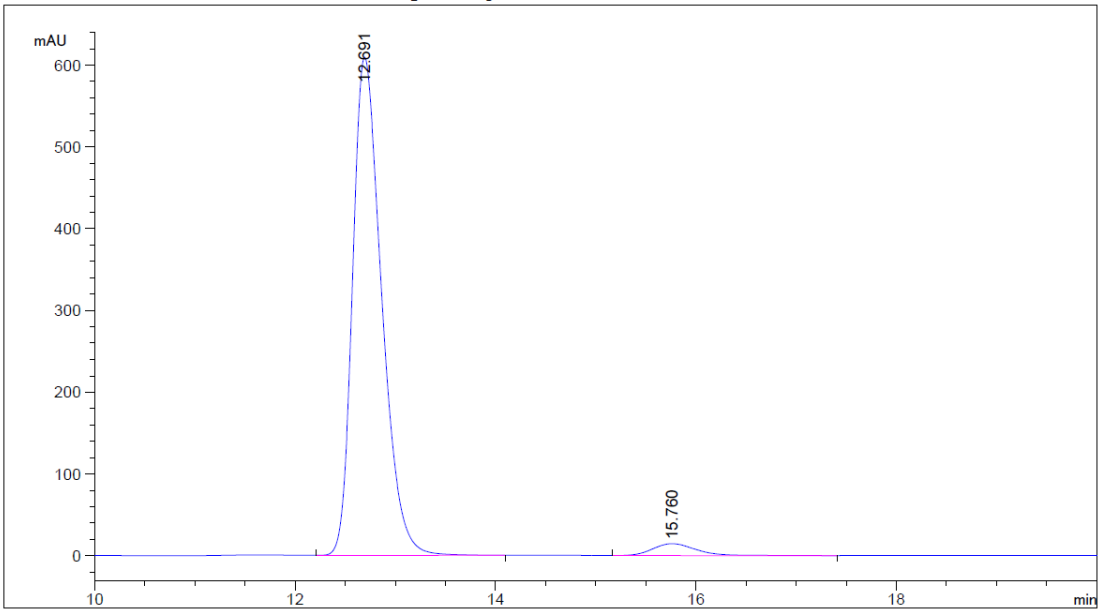
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.259	BB	0.4293	400.07568	14.51475	1.4858
2	20.234	BB	0.5748	2.65259e4	695.05695	98.5142



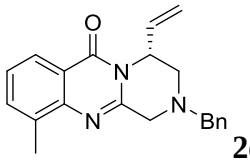
2d



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.755	BB	0.3180	1754.85889	84.51293	50.8412
2	15.662	MM	0.4904	1696.78943	57.66427	49.1588



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.691	VB	0.3085	1.22394e4	609.52209	96.4942
2	15.760	BB	0.4673	444.67914	14.60769	3.5058



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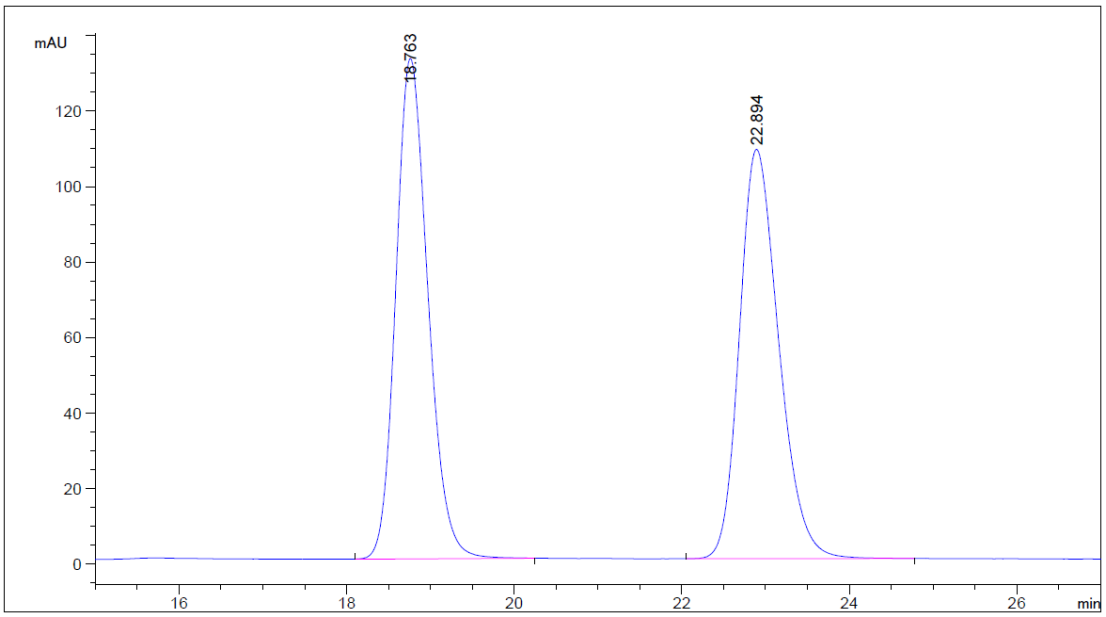
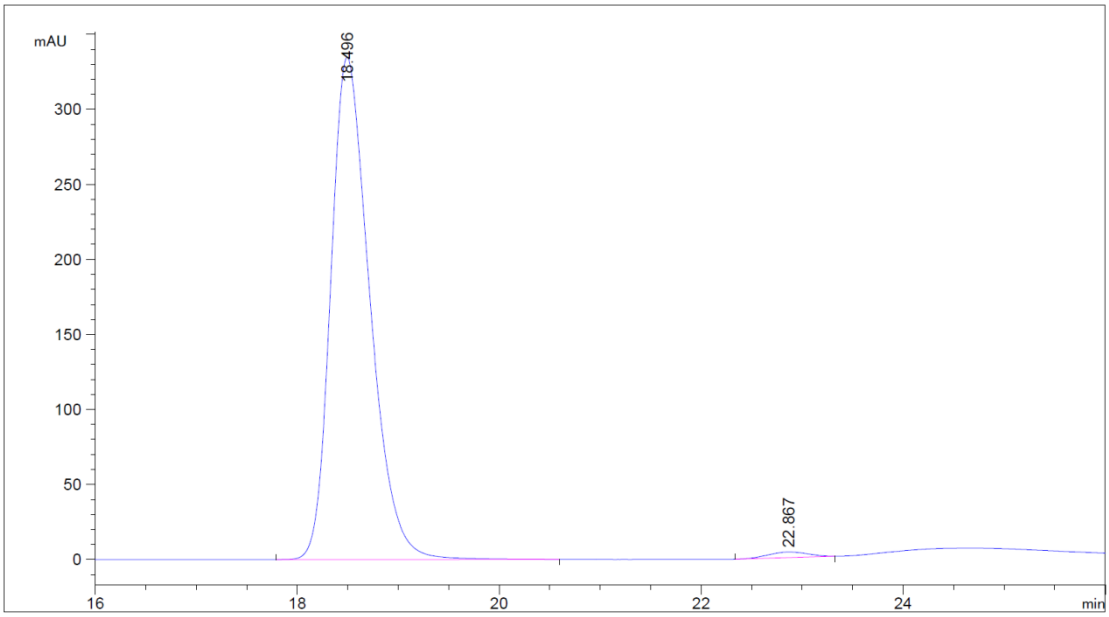
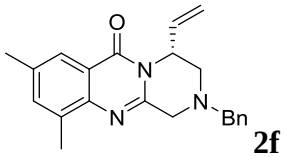


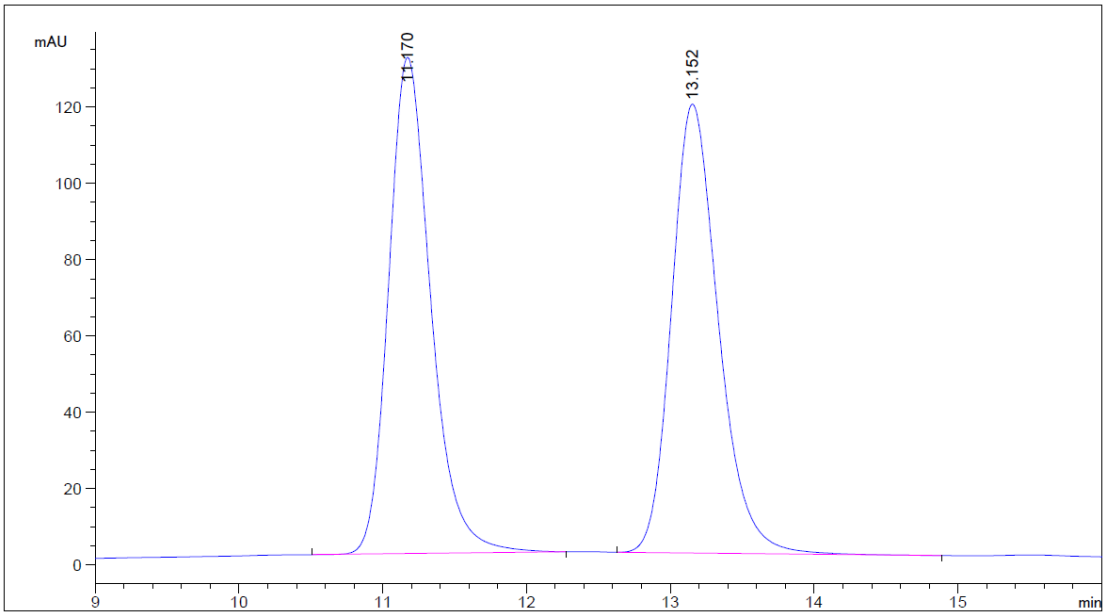
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.763	BB	0.4110	3527.26440	132.52956	49.9568
2	22.894	BB	0.4996	3533.36890	108.42725	50.0432



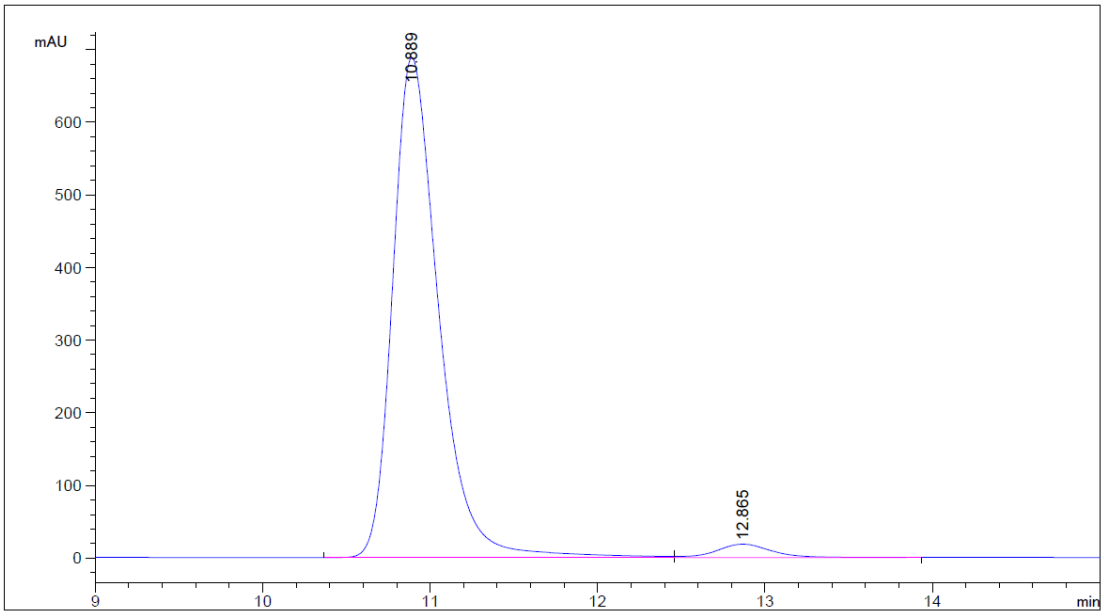
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.496	BB	0.4100	8964.67773	334.72308	98.8648
2	22.867	BB	0.4323	102.93500	3.75010	1.1352



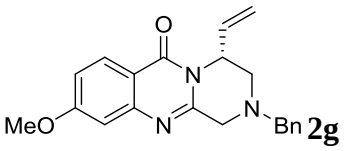
2f



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.170	BB	0.3104	2648.69141	130.03021	49.8247
2	13.152	BB	0.3475	2667.32764	117.63881	50.1753



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.889	BV	0.2919	1.31952e4	688.77795	96.9029
2	12.865	VB	0.3461	421.73480	18.49299	3.0971



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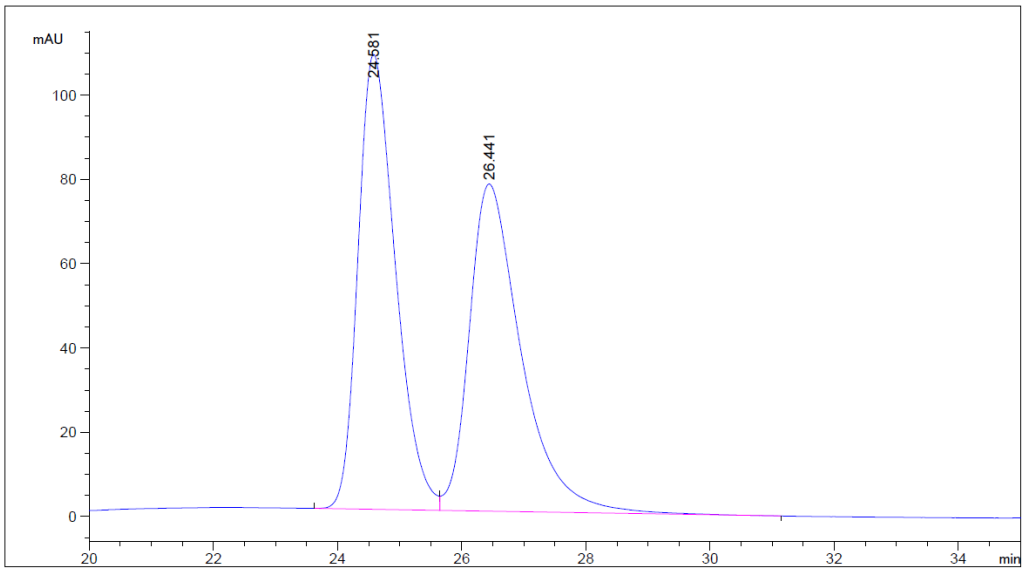
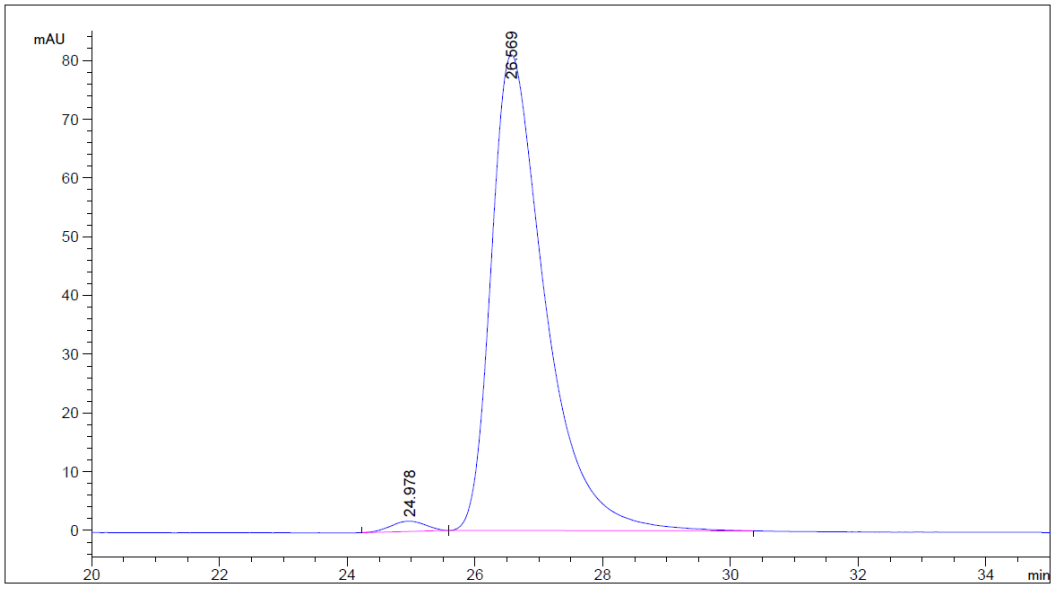
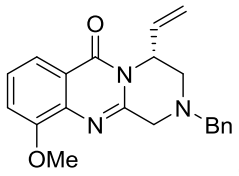


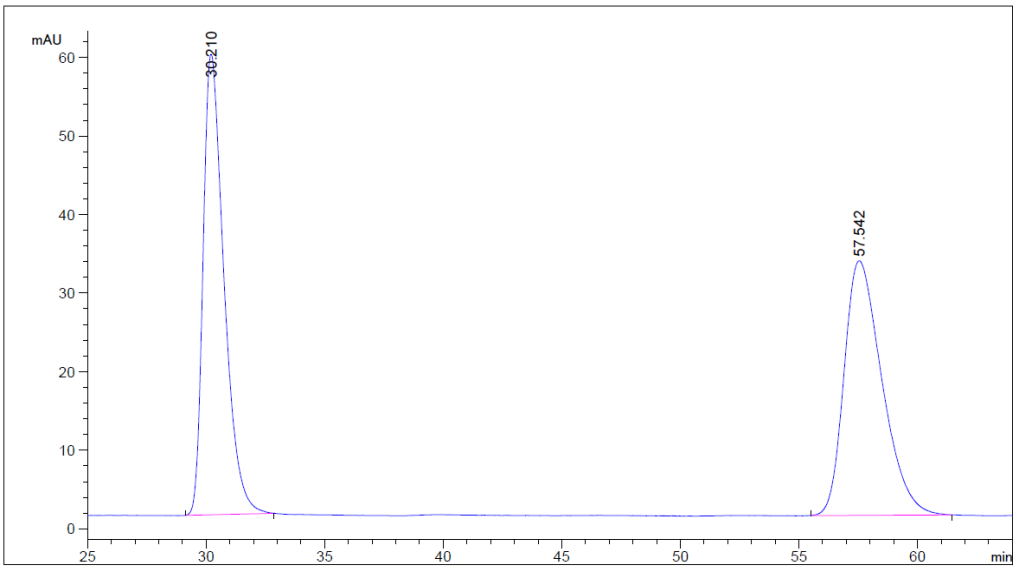
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.581	BV	0.6456	4530.89844	107.91300	50.0083
2	26.441	VB	0.8759	4529.39111	77.61954	49.9917



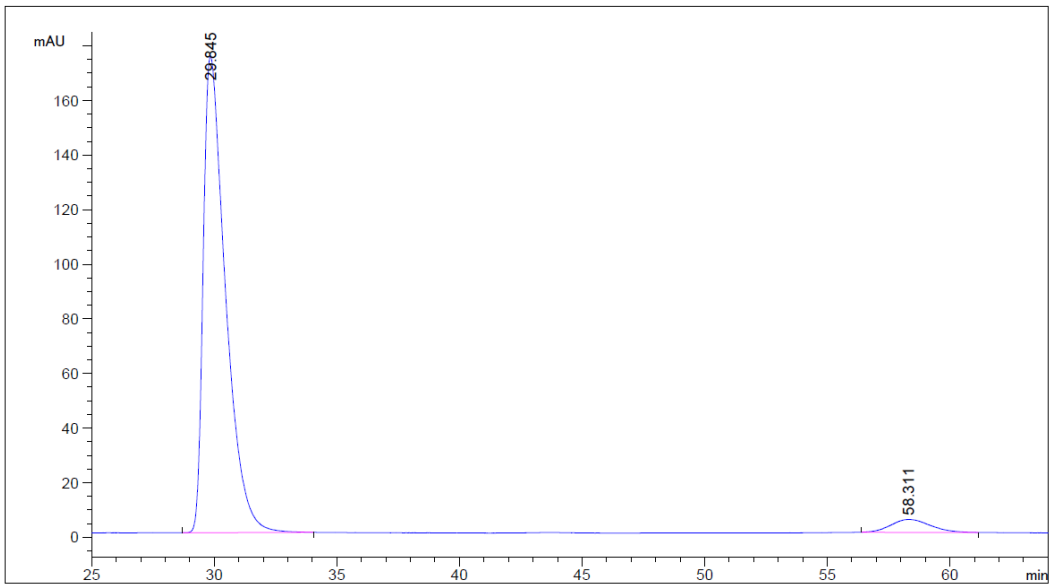
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.978	BB	0.4669	66.26360	1.75990	1.3753
2	26.569	BB	0.8712	4751.83887	80.94640	98.6247



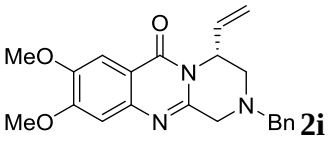
2h



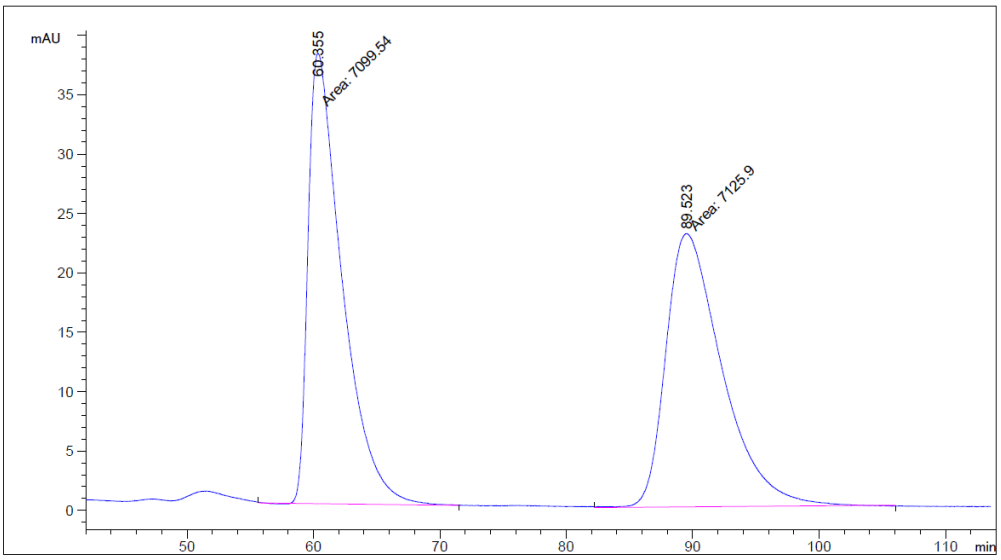
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.210	BB	0.9188	3577.95142	58.62630	49.8963
2	57.542	BB	1.4762	3592.82202	32.42522	50.1037



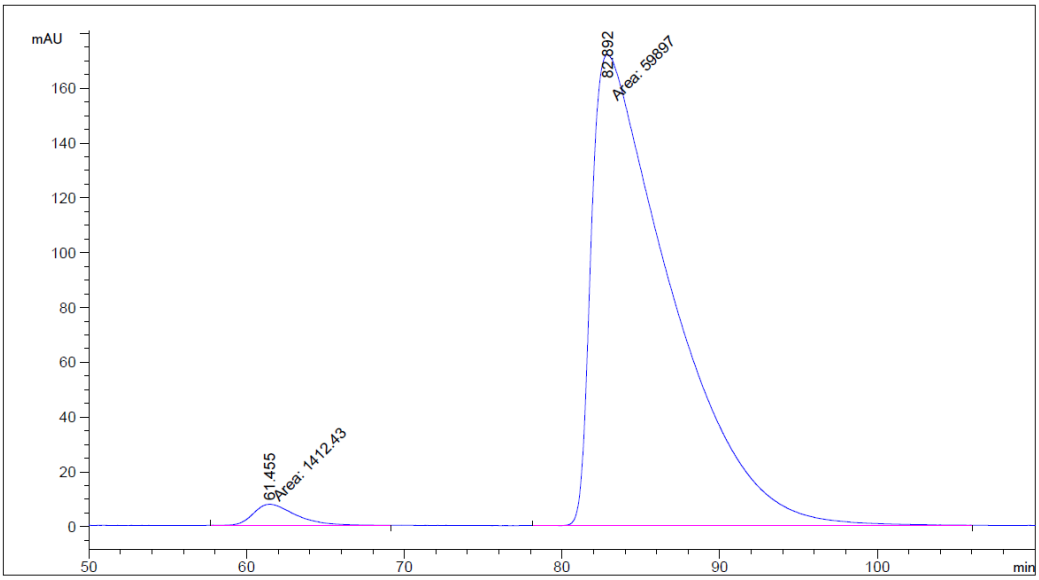
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.845	BB	0.9368	1.09893e4	174.56584	95.4227
2	58.311	BB	1.3098	527.13831	4.74806	4.5773



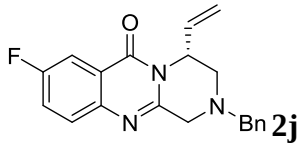
2i



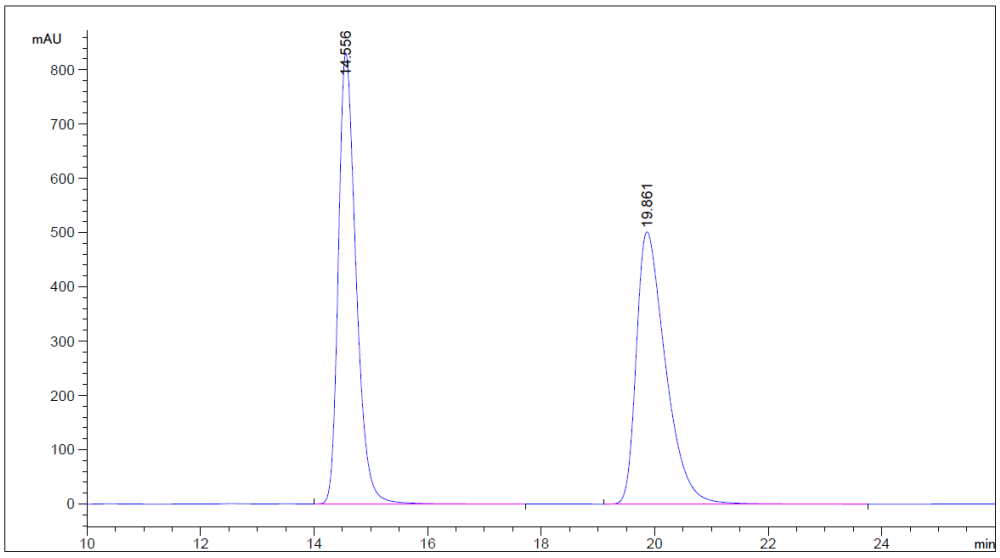
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	60.355	MM	3.1215	7099.53613	37.90615	49.9074
2	89.523	MM	5.1586	7125.89502	23.02274	50.0926



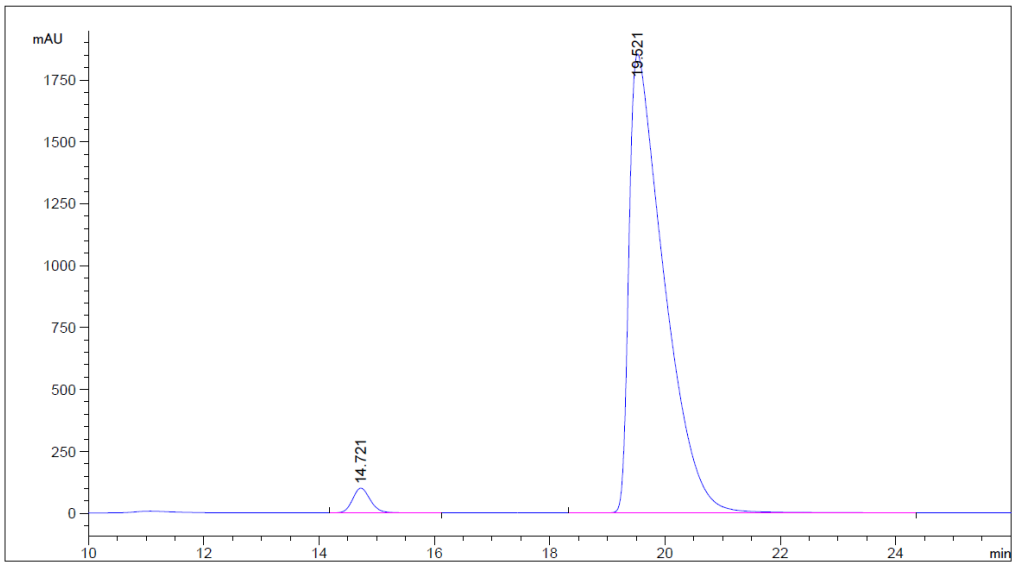
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	61.455	MM	3.0685	1412.43298	7.67180	2.3038
2	82.892	MM	5.8138	5.98970e4	171.71054	97.6962



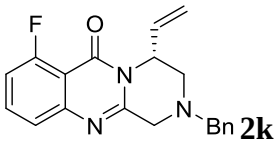
2j



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.556	BB	0.3292	1.79509e4	830.80750	49.9869
2	19.861	BB	0.5398	1.79603e4	501.89597	50.0131



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.721	BB	0.3280	2131.89307	99.74544	2.6638
2	19.521	BB	0.6129	7.78993e4	1852.65747	97.3362



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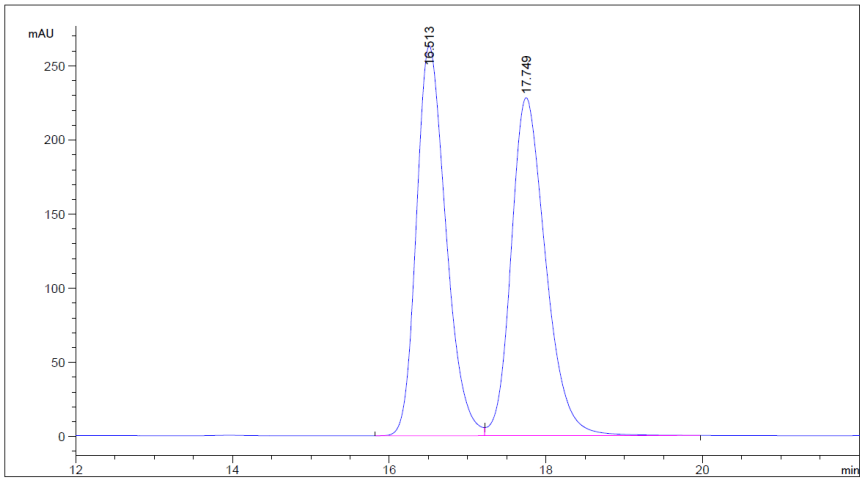
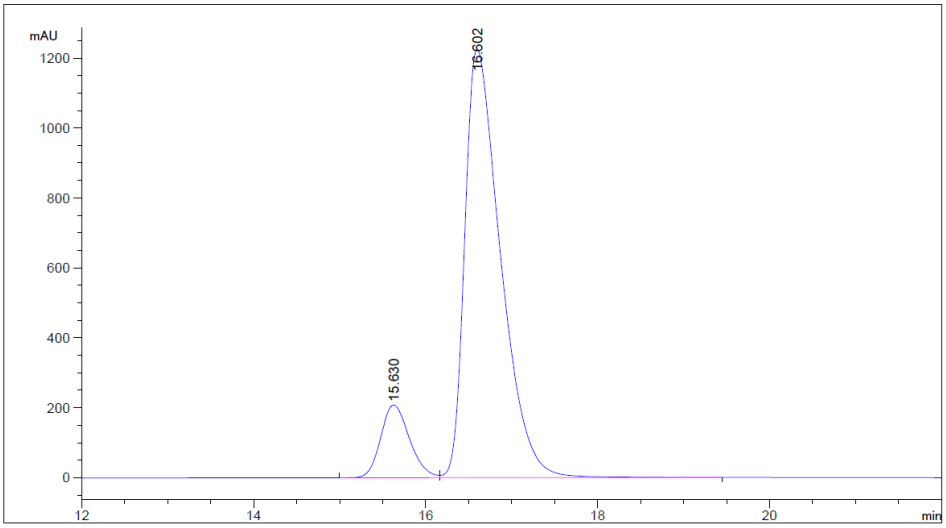


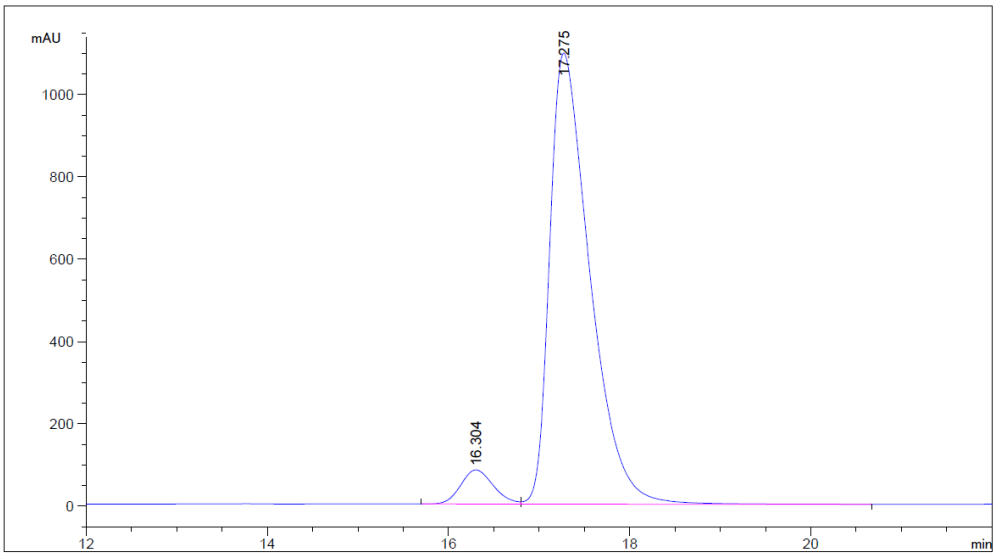
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.513	BV	0.4010	6876.77686	263.11102	49.6921
2	17.749	VB	0.4669	6961.99121	227.97049	50.3079

Using (*R*)-**B** as the ligand



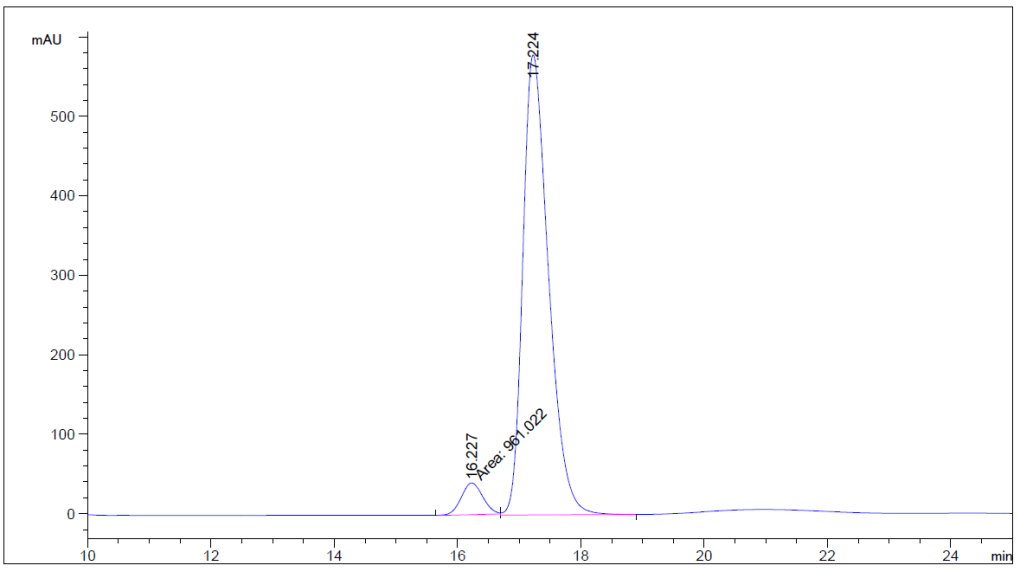
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.630	BV	0.3603	4840.98047	208.07271	12.0499
2	16.602	VB	0.4370	3.53336e4	1224.99084	87.9501

Using (*R*)-**C** as the ligand

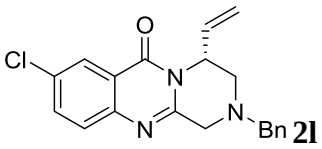


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.304	BV	0.3859	2074.59497	83.11056	5.7863
2	17.275	VB	0.4645	3.37788e4	1095.75842	94.2137

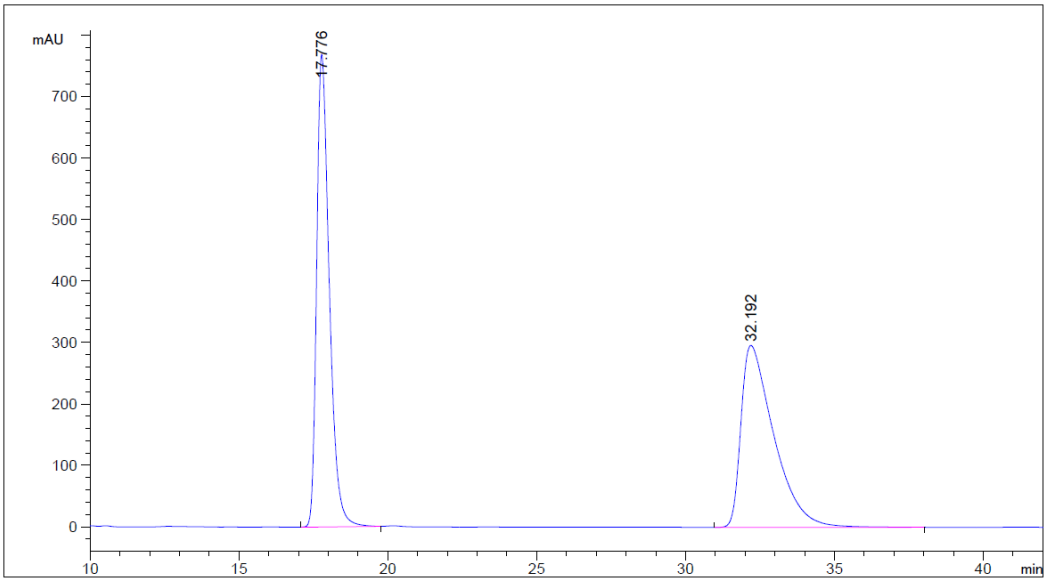
Using (*R*)-**D** as the ligand



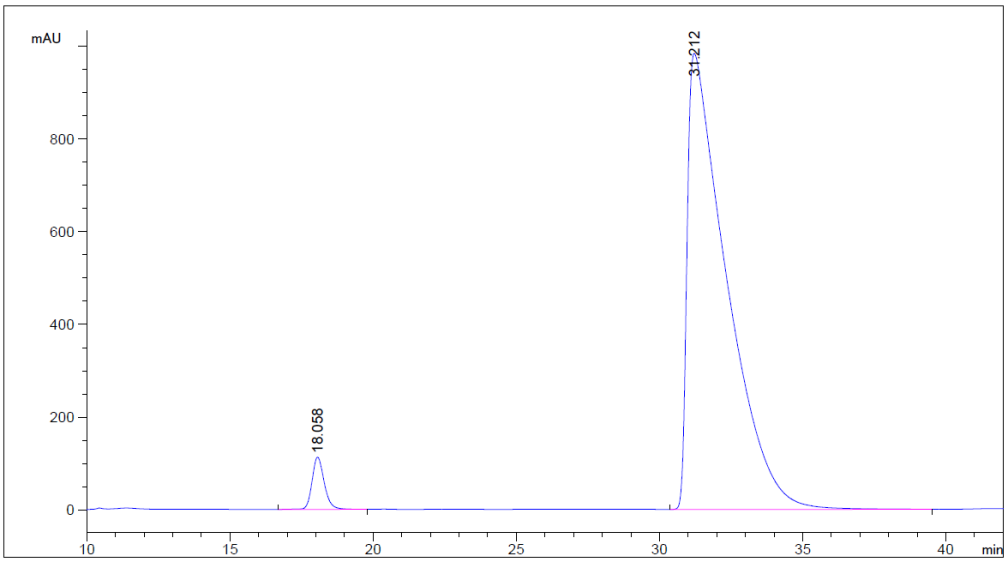
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.227	MM	0.4031	961.02246	39.73347	5.4326
2	17.224	VB	0.4436	1.67289e4	578.66736	94.5674



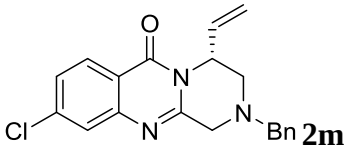
2l



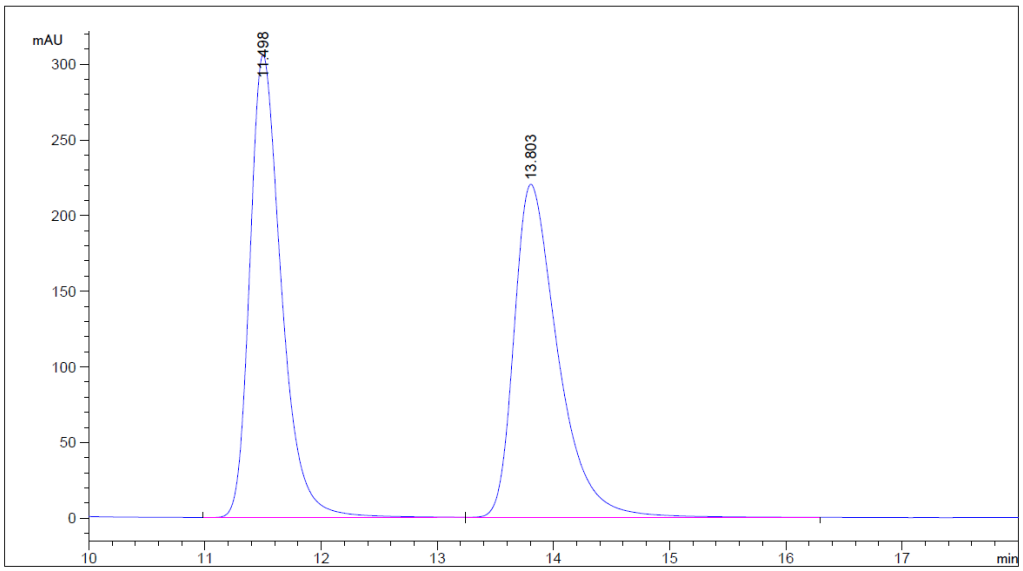
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.776	BB	0.4470	2.26470e4	768.92737	49.8738
2	32.192	BB	1.1239	2.27617e4	296.12753	50.1262



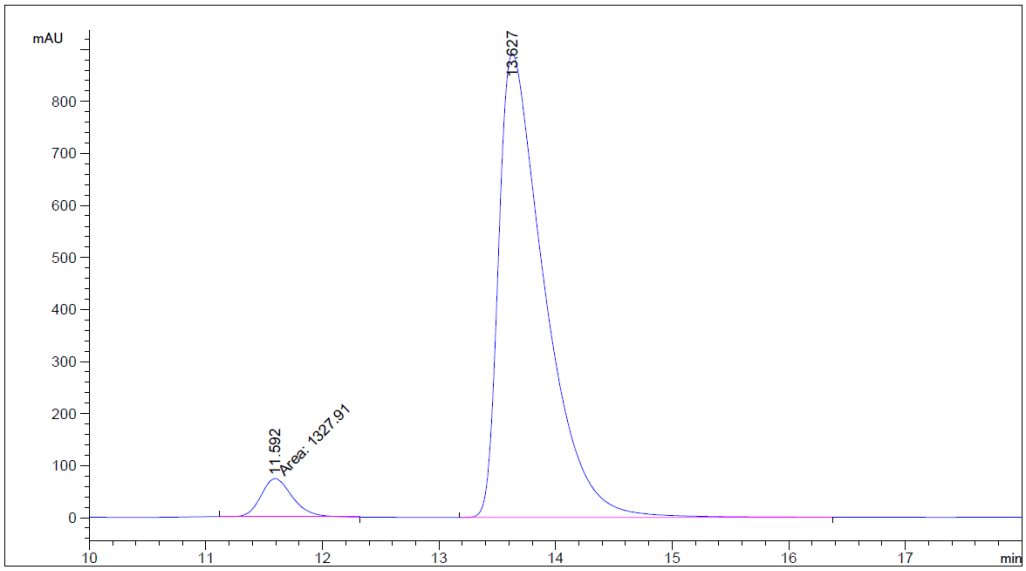
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.058	BB	0.4555	3341.38110	112.57658	3.4437
2	31.212	BB	1.3183	9.36864e4	983.34247	96.5563



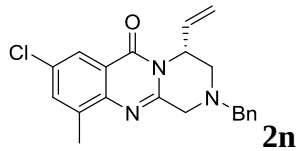
2m



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.498	BB	0.2872	5775.81299	305.97177	49.9988
2	13.803	BB	0.3965	5776.09424	220.07407	50.0012



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.592	MM	0.3056	1327.90613	72.42086	5.1823
2	13.627	BB	0.4024	2.42962e4	891.45215	94.8177



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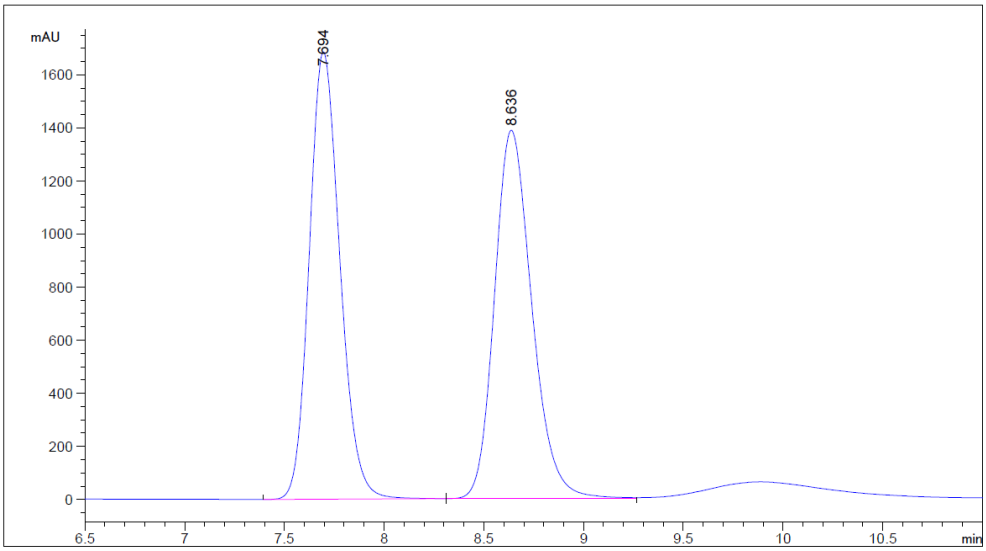
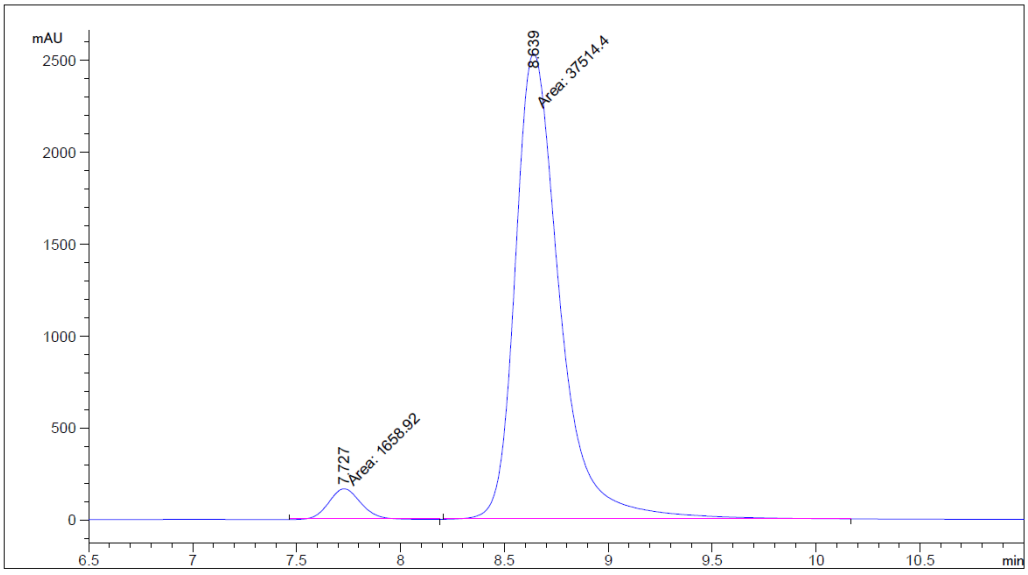
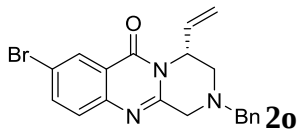


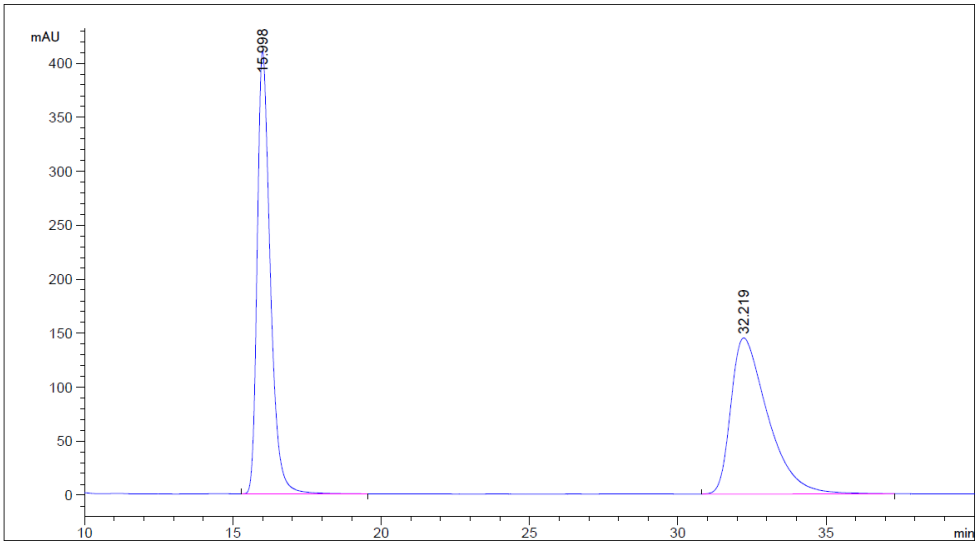
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.694	BB	0.1653	1.80027e4	1686.11157	49.8717
2	8.636	BV	0.2016	1.80953e4	1388.26746	50.1283



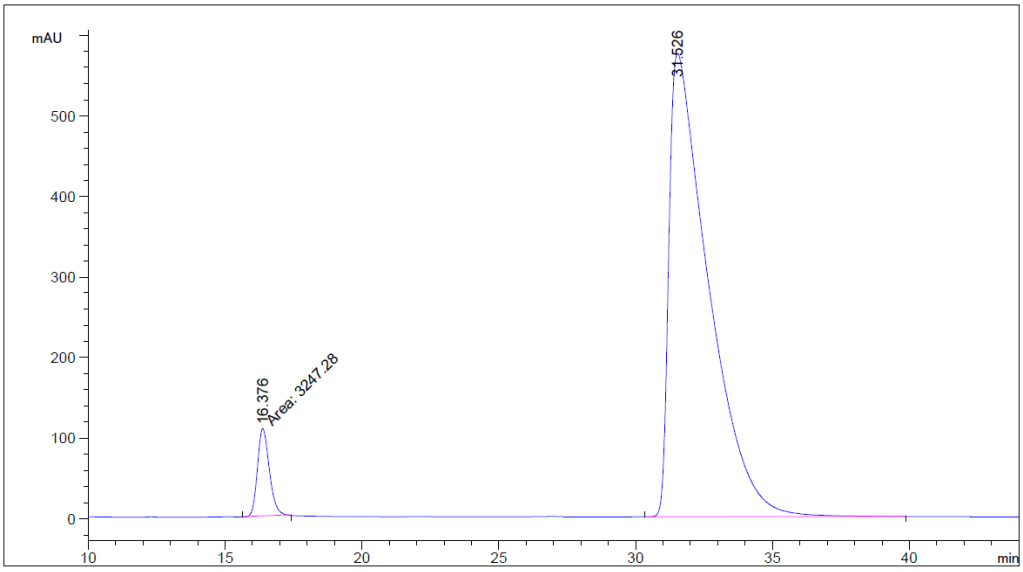
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.727	MM	0.1711	1658.91821	161.59183	4.2348
2	8.639	MM	0.2470	3.75144e4	2530.92700	95.7652



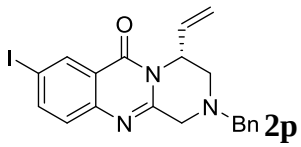
2o



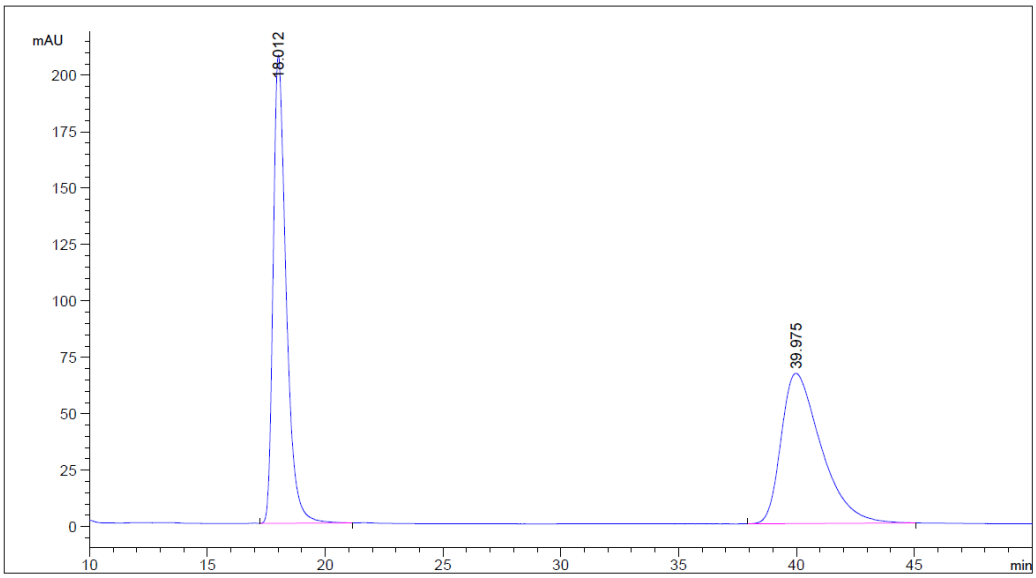
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.998	BB	0.4645	1.25557e4	410.57648	50.1298
2	32.219	BB	1.2920	1.24907e4	144.55751	49.8702



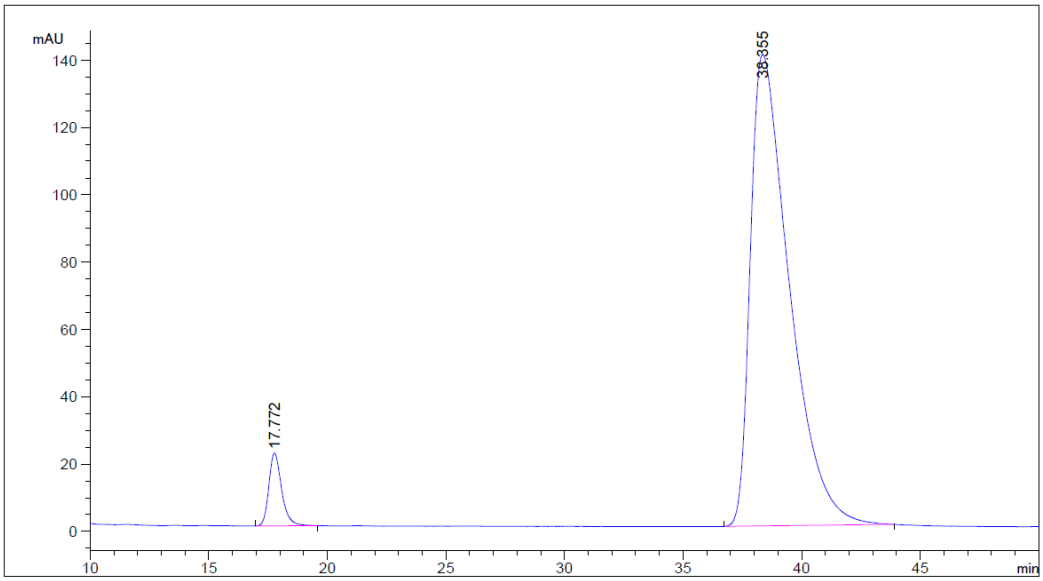
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.376	MM	0.5004	3247.27588	108.15260	5.3578
2	31.526	BB	1.4092	5.73613e4	574.64471	94.6422



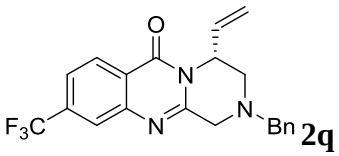
2p



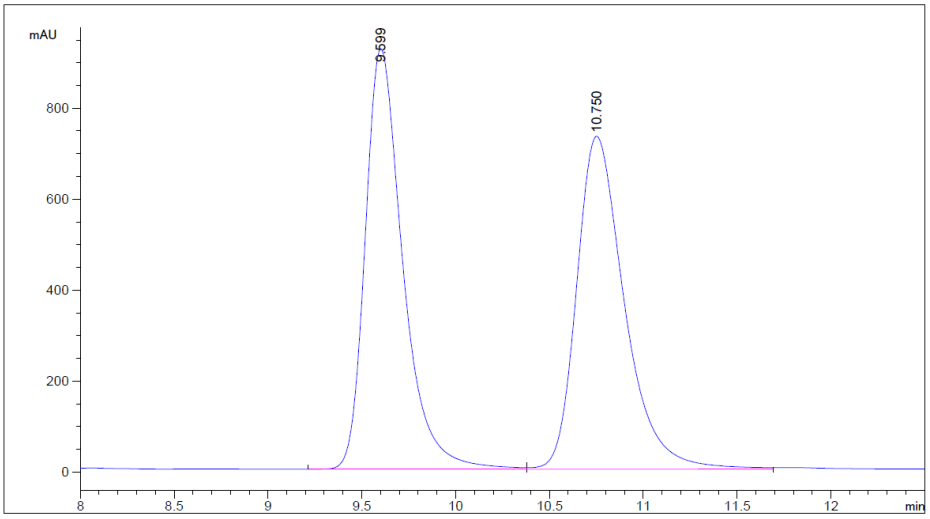
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.012	BB	0.5793	7945.62598	207.47342	50.2790
2	39.975	BB	1.7222	7857.43115	66.56643	49.7210



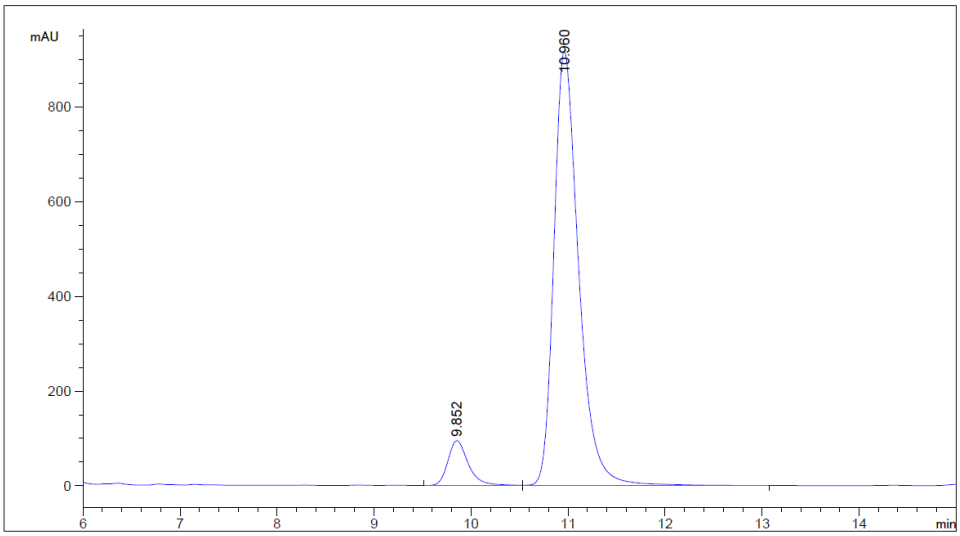
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.772	BB	0.5718	807.41614	21.58713	4.8026
2	38.355	BB	1.6415	1.60047e4	140.09555	95.1974



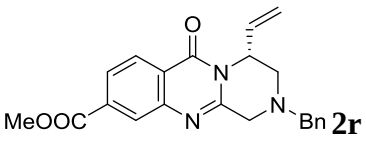
2q



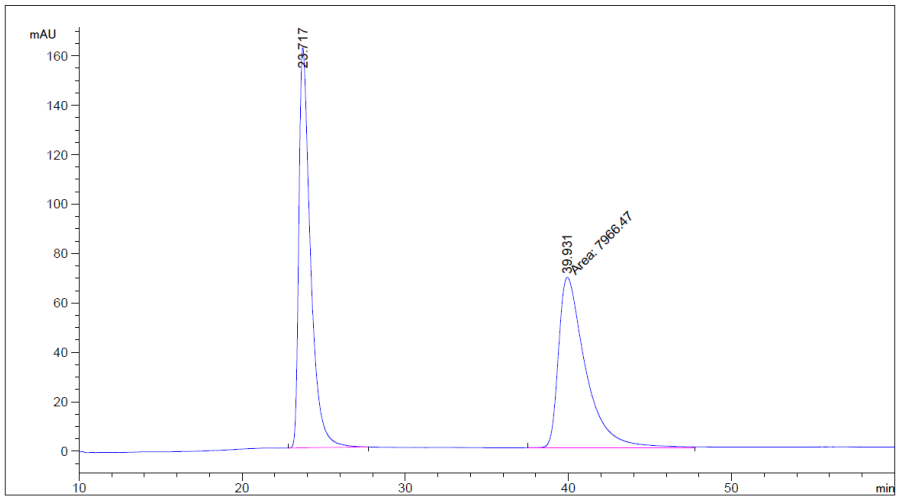
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.599	BV	0.2105	1.28883e4	925.40594	49.8129
2	10.750	VV	0.2695	1.29851e4	732.36218	50.1871



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.852	BV	0.2220	1389.85376	94.79605	7.8662
2	10.960	VB	0.2695	1.62789e4	917.79321	92.1338

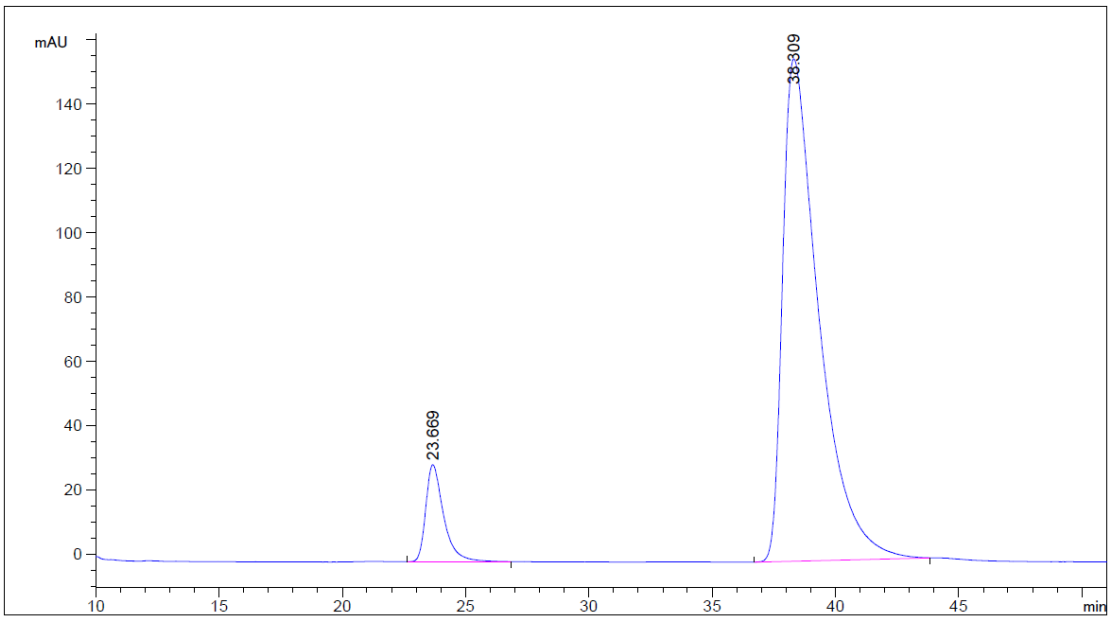


2r



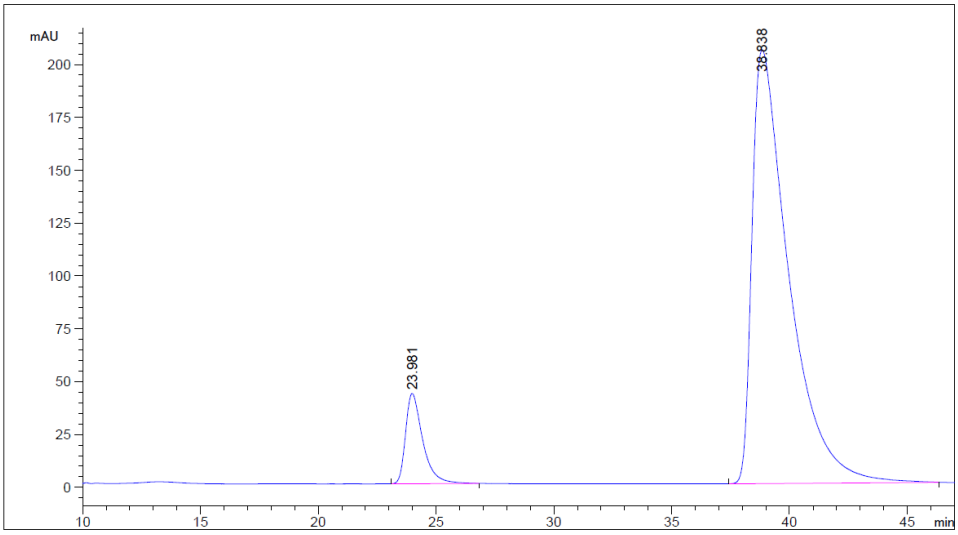
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.717	BB	0.7370	8006.61182	161.94460	50.1257
2	39.931	MM	1.9254	7966.46924	68.96098	49.8743

Using (*R*)-**B** as the ligand



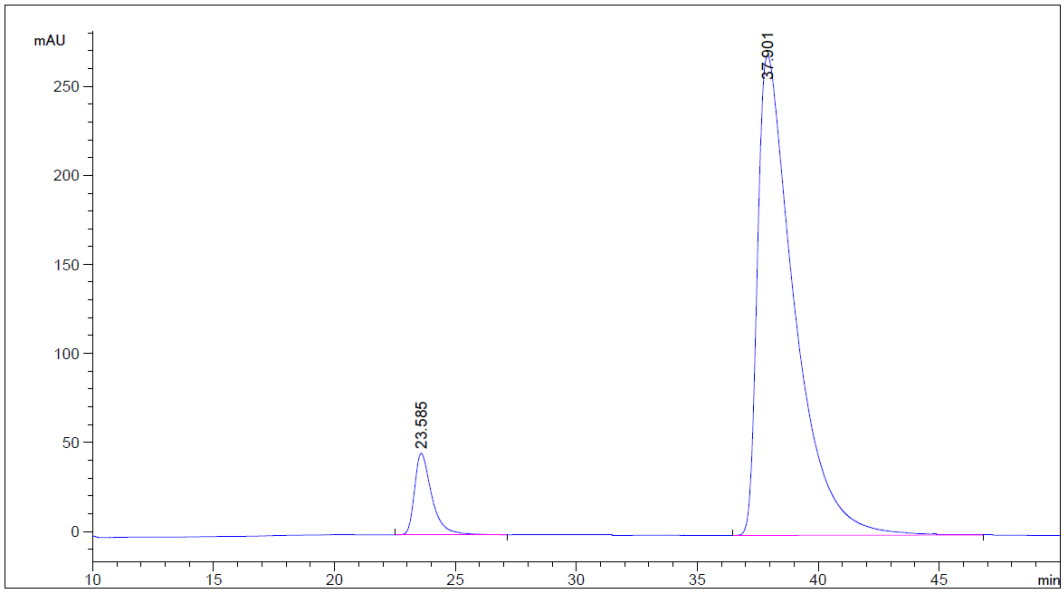
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.669	BB	0.7493	1518.54688	30.14844	8.6762
2	38.309	BB	1.4960	1.59838e4	156.28470	91.3238

Using (*R*)-**C** as the ligand

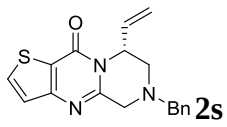


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.981	BB	0.7544	2164.18188	42.69686	8.8493
2	38.838	BB	1.5730	2.22919e4	205.23135	91.1507

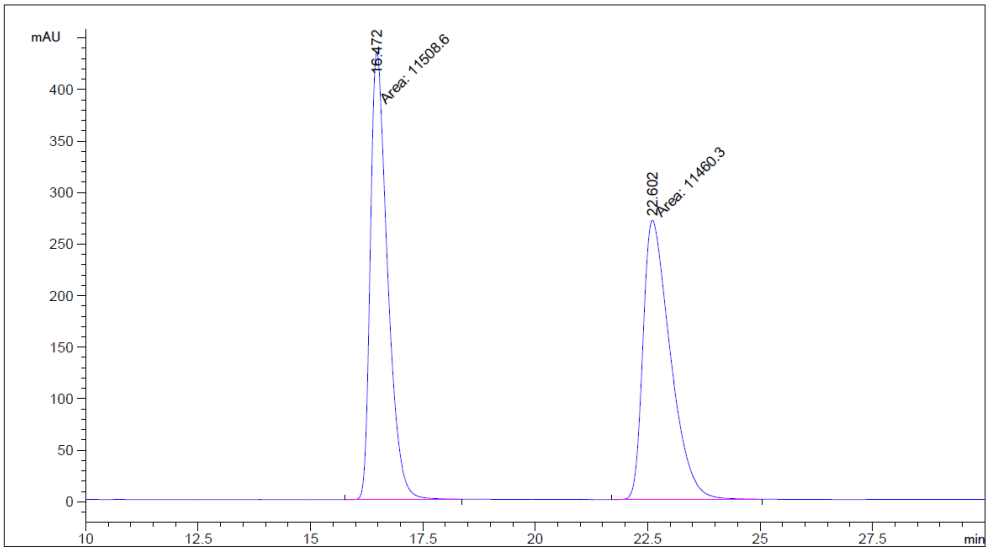
Using (*R*)-**D** as the ligand



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.585	BB	0.7425	2280.75146	45.80953	7.4107
2	37.901	BB	1.5213	2.84956e4	269.63327	92.5893

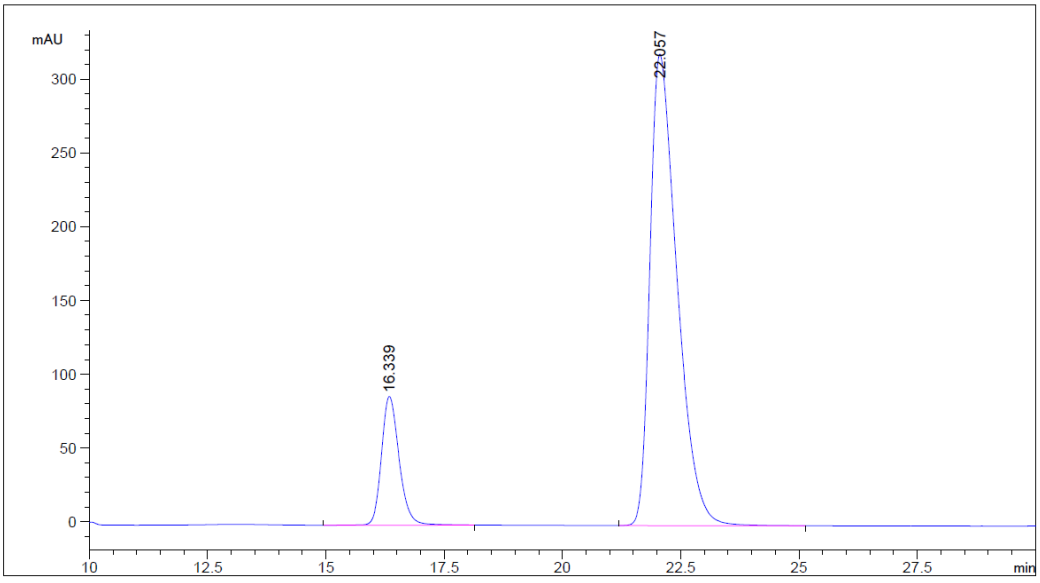


2s



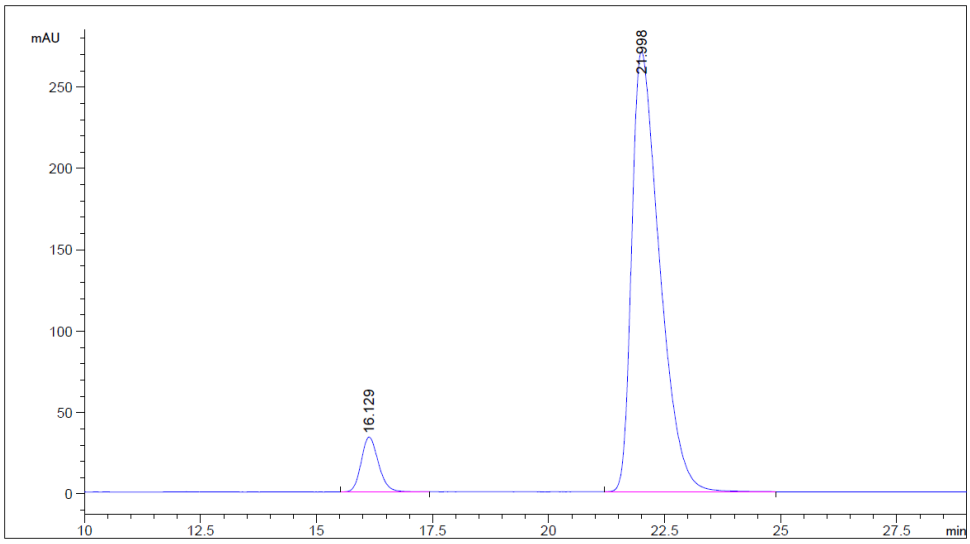
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.472	MM	0.4418	1.15086e4	434.11124	50.1052
2	22.602	MM	0.7046	1.14603e4	271.09335	49.8948

Using (*R*)-**B** as the ligand



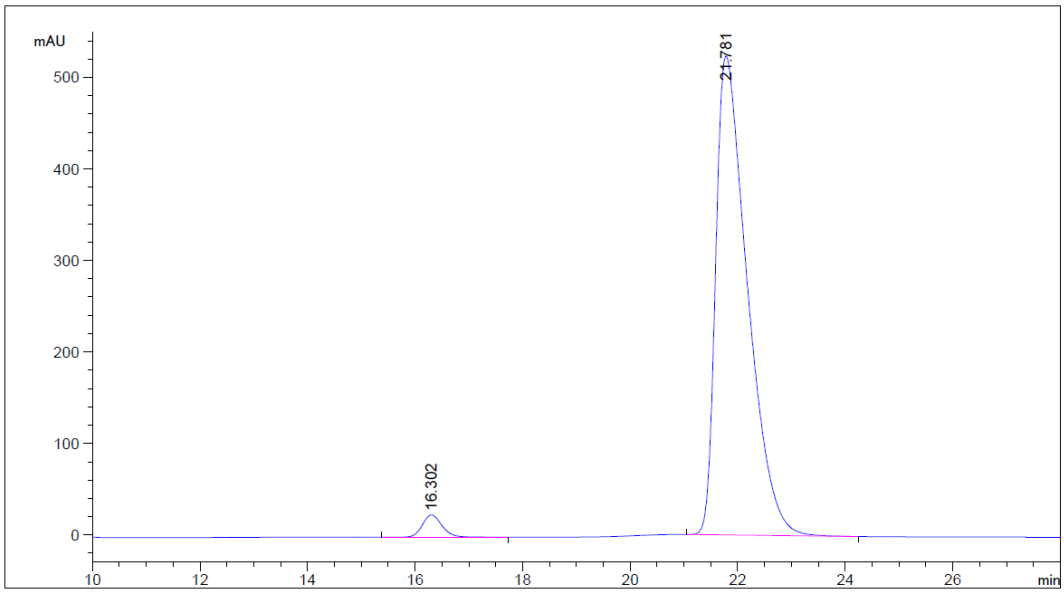
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.339	BB	0.3971	2263.99609	87.31680	15.1081
2	22.057	BB	0.6055	1.27213e4	319.68109	84.8919

Using (*R*)-**C** as the ligand

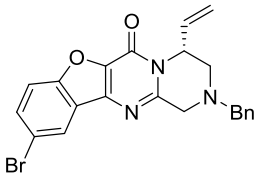


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.129	BB	0.4010	871.99628	33.69035	7.1727
2	21.998	BB	0.6311	1.12851e4	270.36655	92.8273

Using (*R*)-**D** as the ligand



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.302	BB	0.3939	624.90326	24.35786	2.8473
2	21.781	BB	0.6124	2.13224e4	523.11627	97.1527



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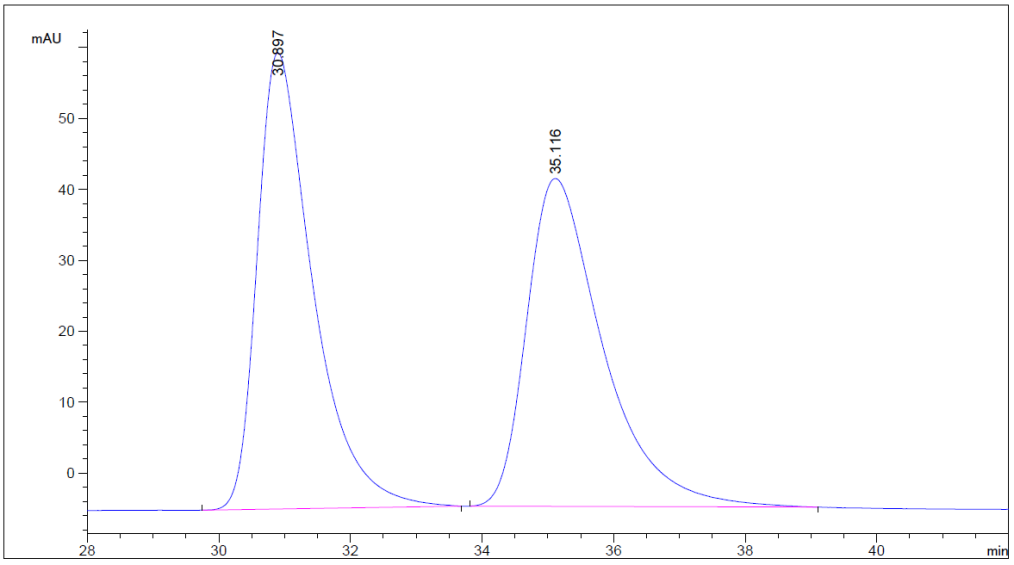
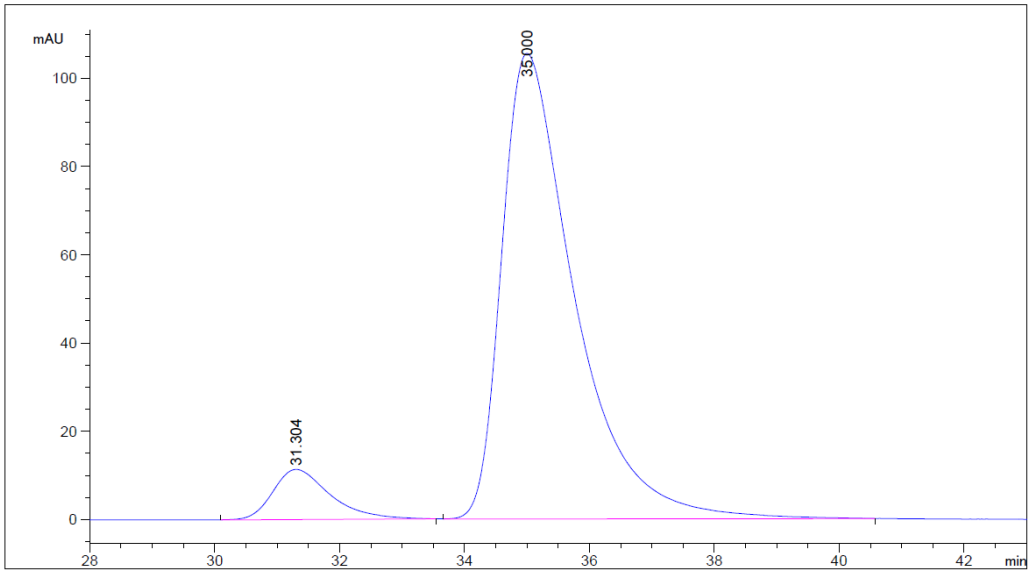
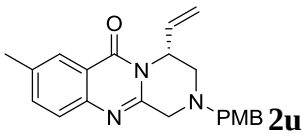


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.897	BB	0.8796	3778.36499	64.26614	50.4052
2	35.116	BB	1.1651	3717.61279	46.16713	49.5948



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	31.304	BB	0.8875	722.59277	11.36357	7.7897
2	35.000	BB	1.1935	8553.70508	105.49239	92.2103



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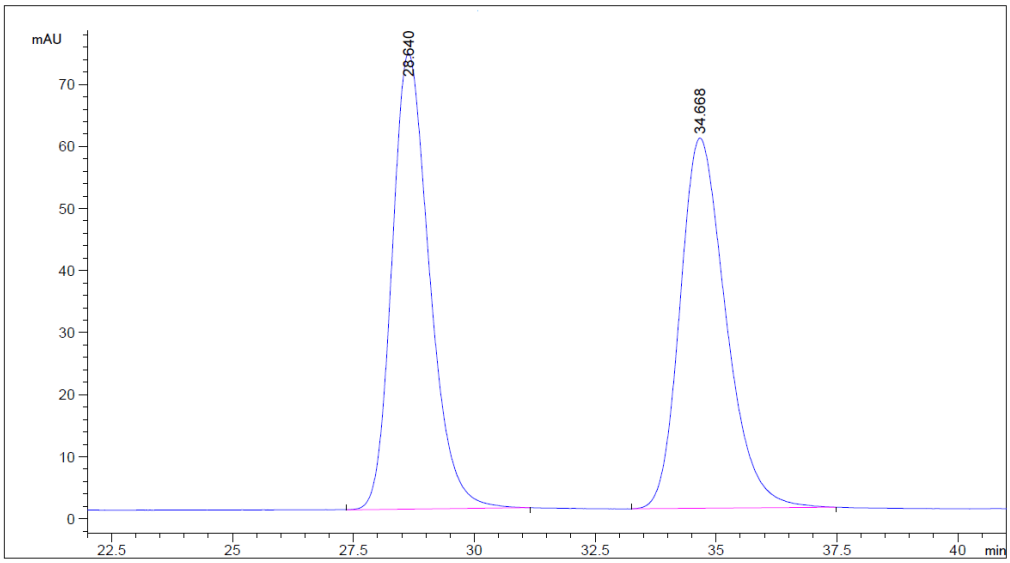
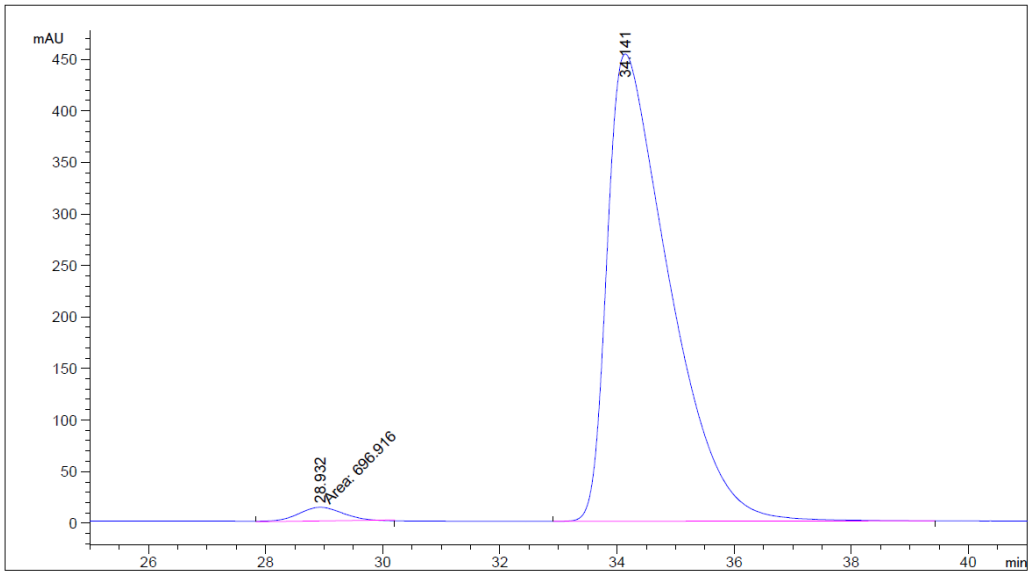
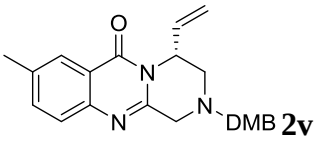


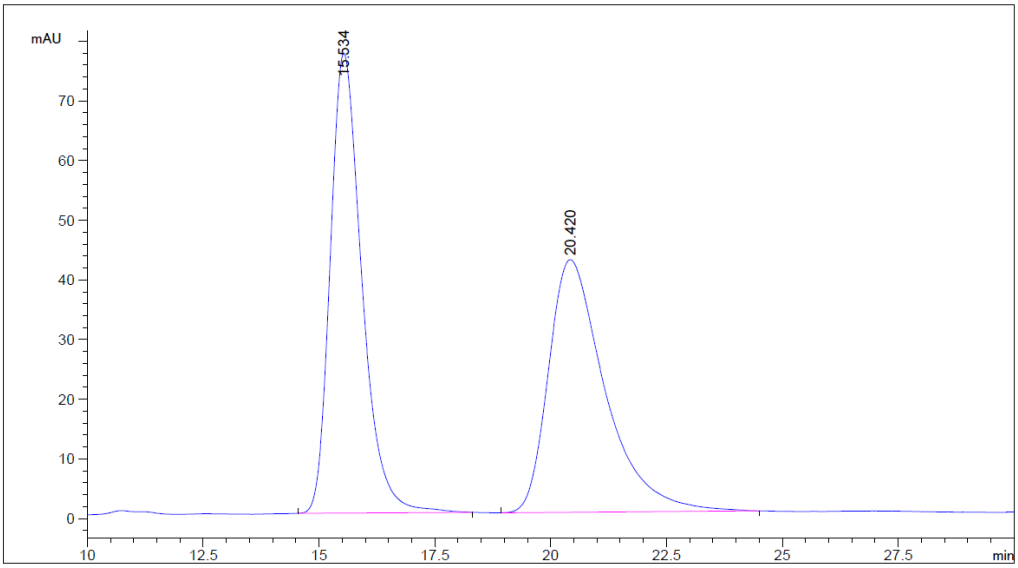
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.640	BB	0.8285	3949.92432	73.42418	50.1173
2	34.668	BB	0.9828	3931.43530	59.65998	49.8827



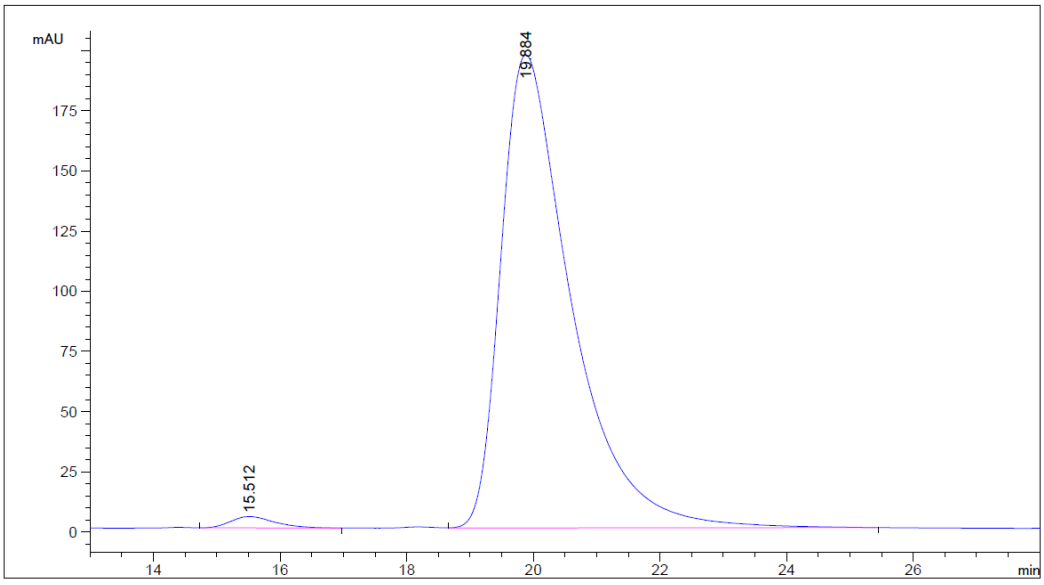
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.932	MM	0.8758	696.91589	13.26221	2.0506
2	34.141	BB	1.0633	3.32890e4	453.43622	97.9494



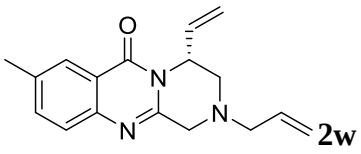
2v

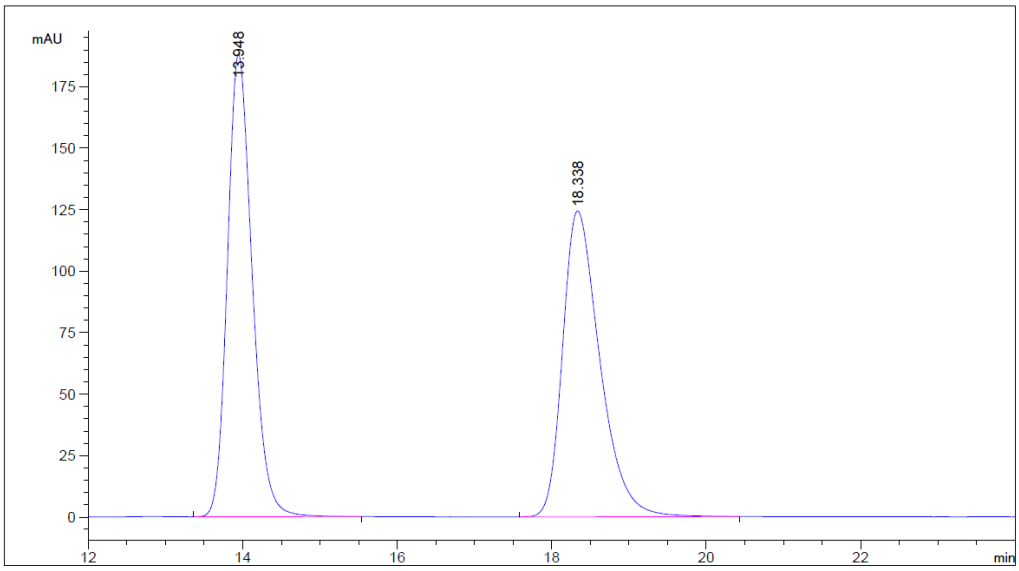


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.534	BB	0.7216	3653.11792	77.10745	50.4701
2	20.420	BB	1.2194	3585.07104	42.33620	49.5299

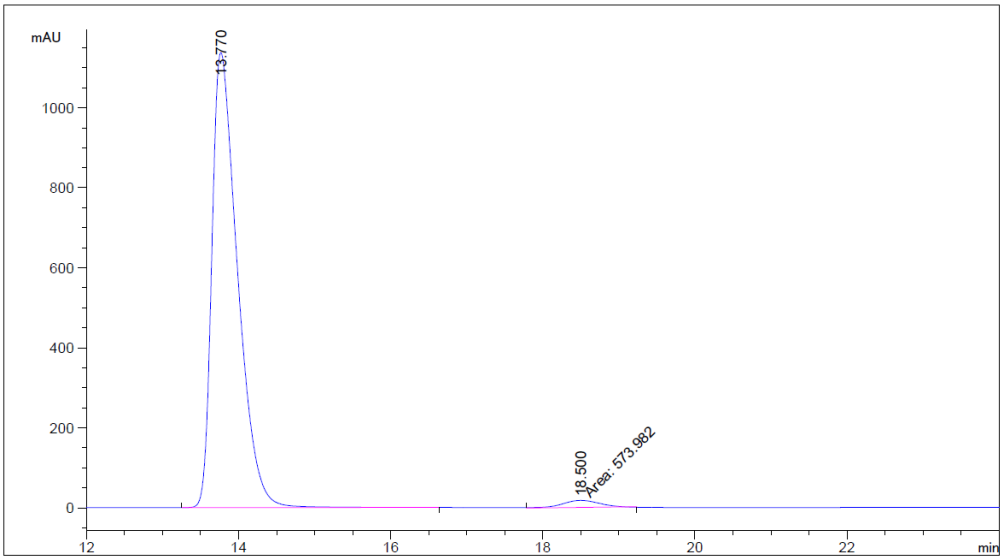


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.512	BB	0.6676	226.44688	4.71866	1.4688
2	19.884	VB	1.1301	1.51911e4	196.60155	98.5312

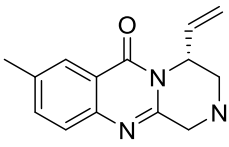




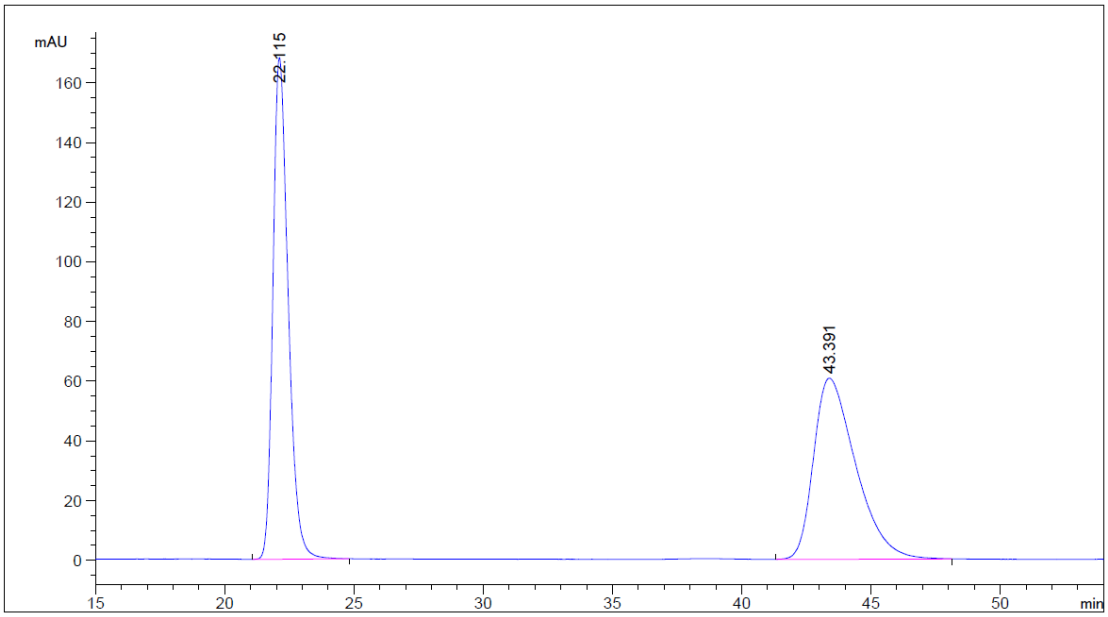
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.948	BB	0.3412	4186.64355	188.09834	50.1084
2	18.338	BB	0.5089	4168.53027	124.40487	49.8916



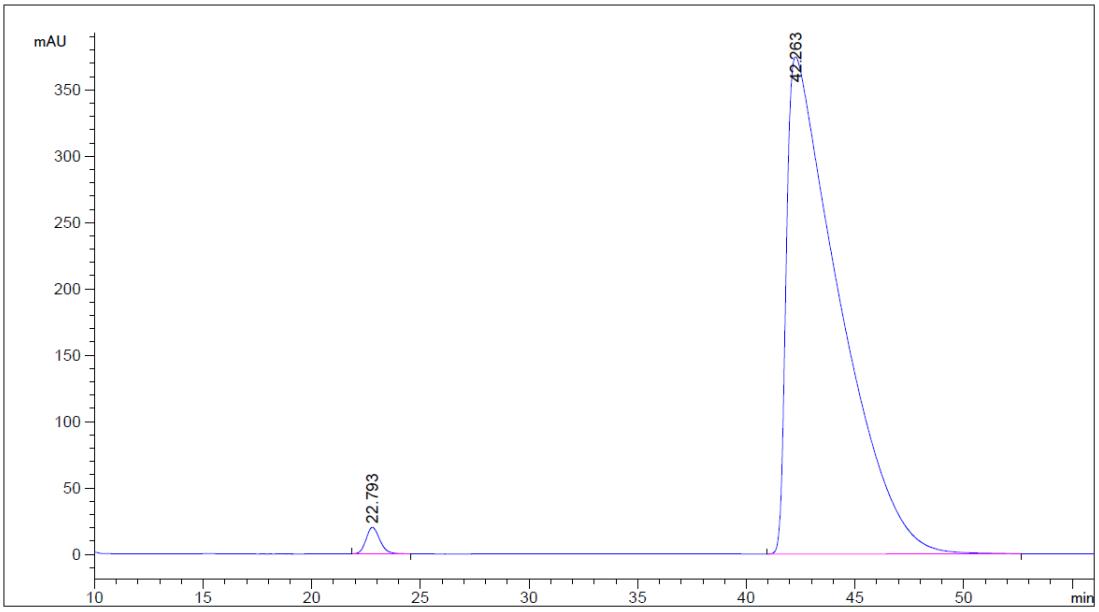
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.770	BB	0.3527	2.65948e4	1137.92065	97.8873
2	18.500	MM	0.5462	573.98212	17.51546	2.1127



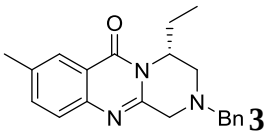
2a in large scale



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.115	BB	0.6287	6897.43555	168.10358	50.0978
2	43.391	BB	1.6042	6870.49609	60.64320	49.9022



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.793	BB	0.6815	881.89227	19.95867	1.3790
2	42.263	BB	2.2391	6.30708e4	374.38660	98.6210



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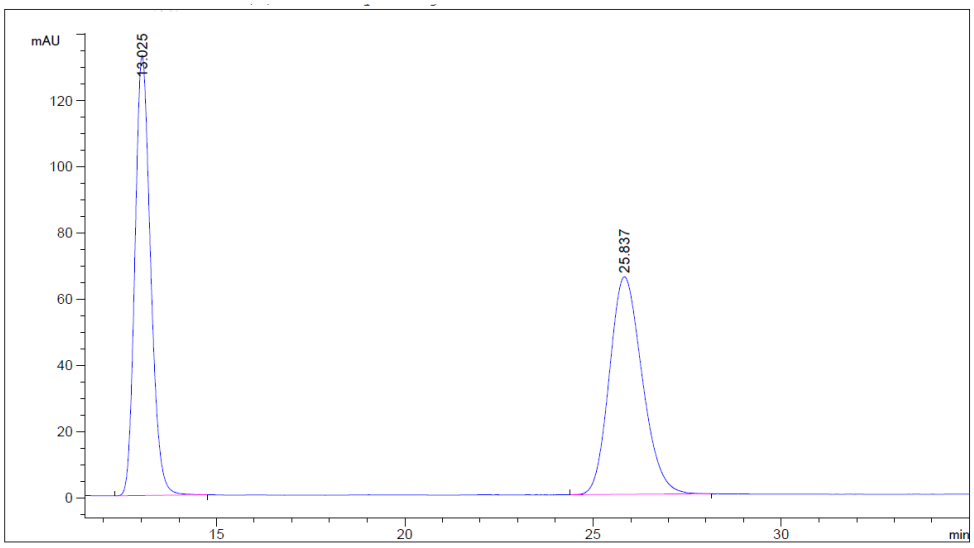
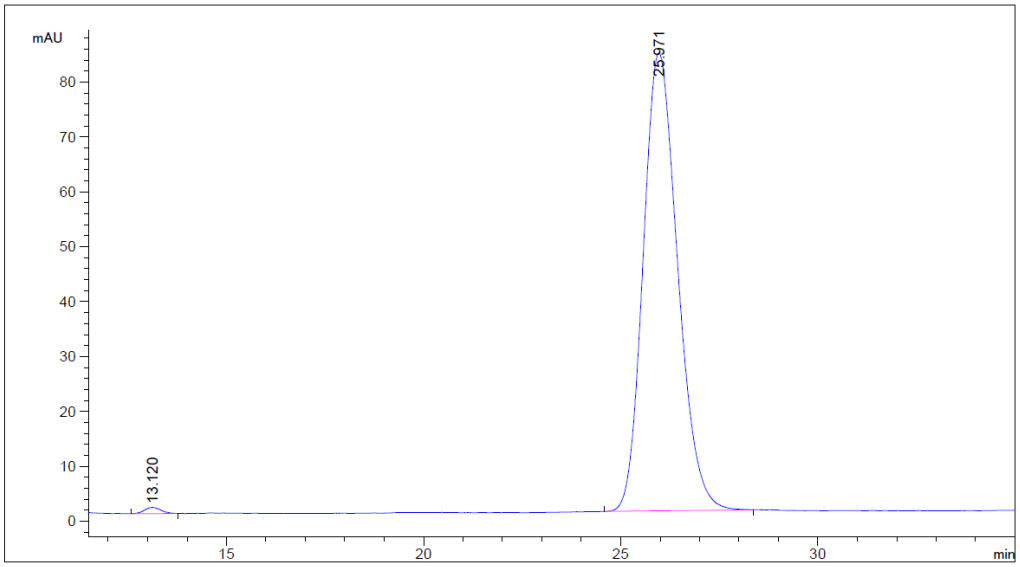
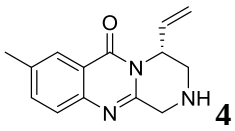


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.025	BB	0.4459	3834.89771	132.88718	49.1054
2	25.837	BB	0.9345	3974.62305	65.68696	50.8946



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.120	BB	0.3553	32.61367	1.13112	0.6406
2	25.971	BB	0.9335	5058.49023	83.37899	99.3594



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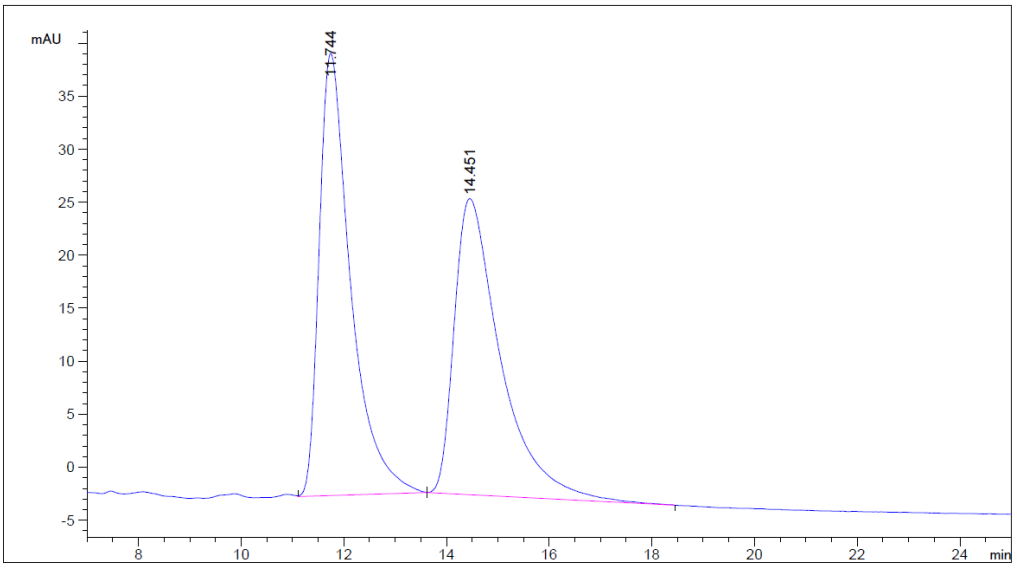
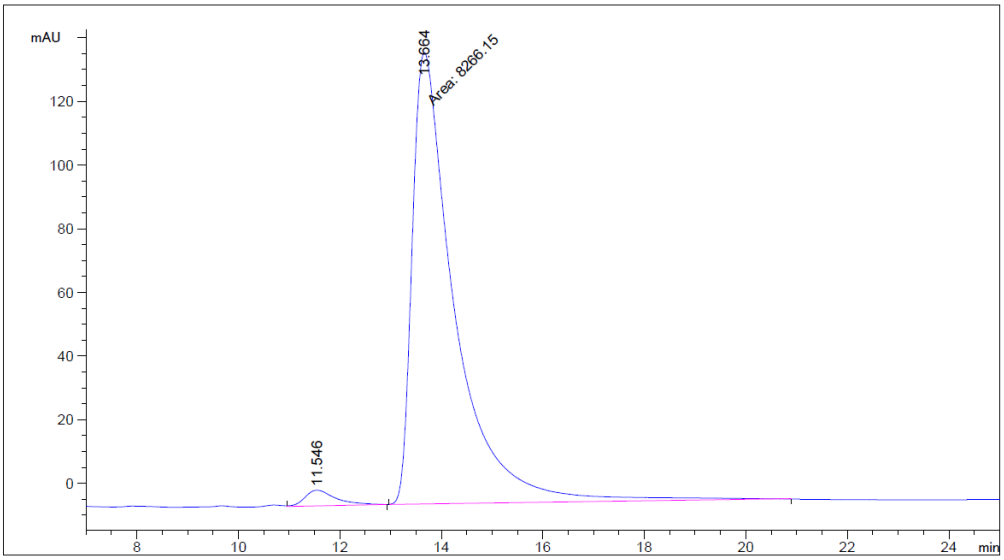
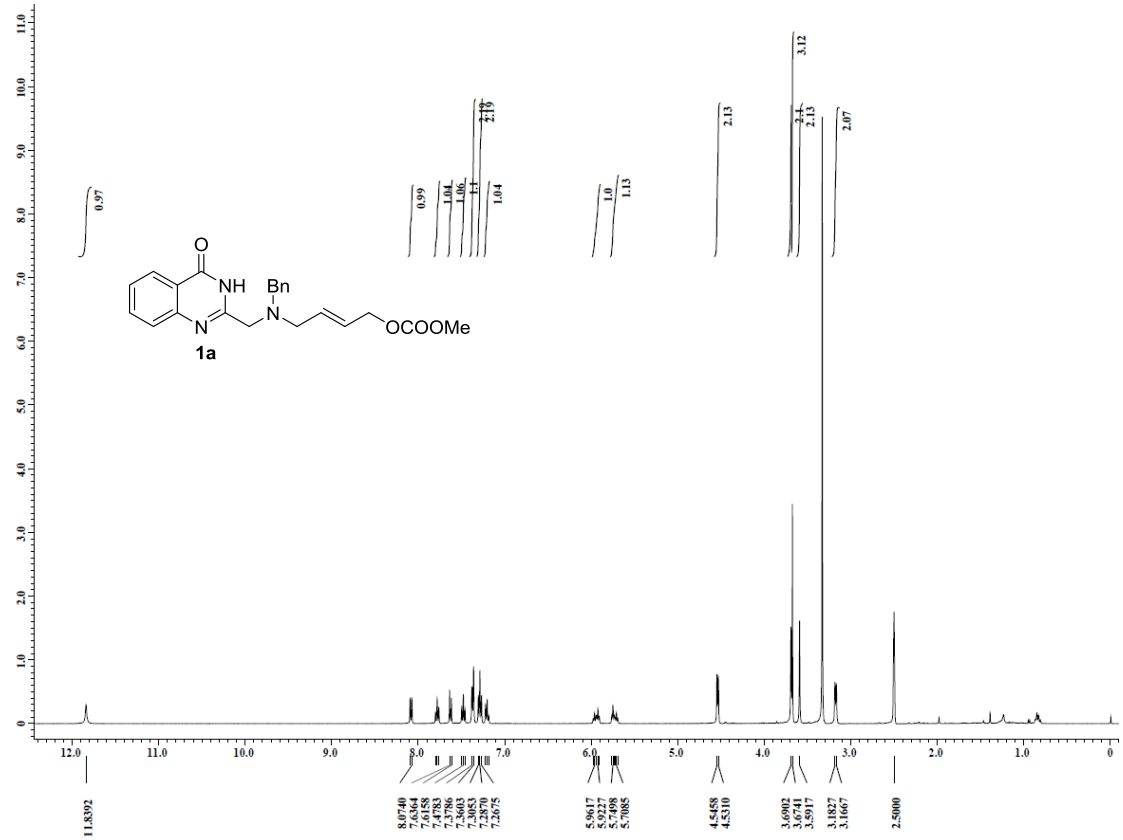


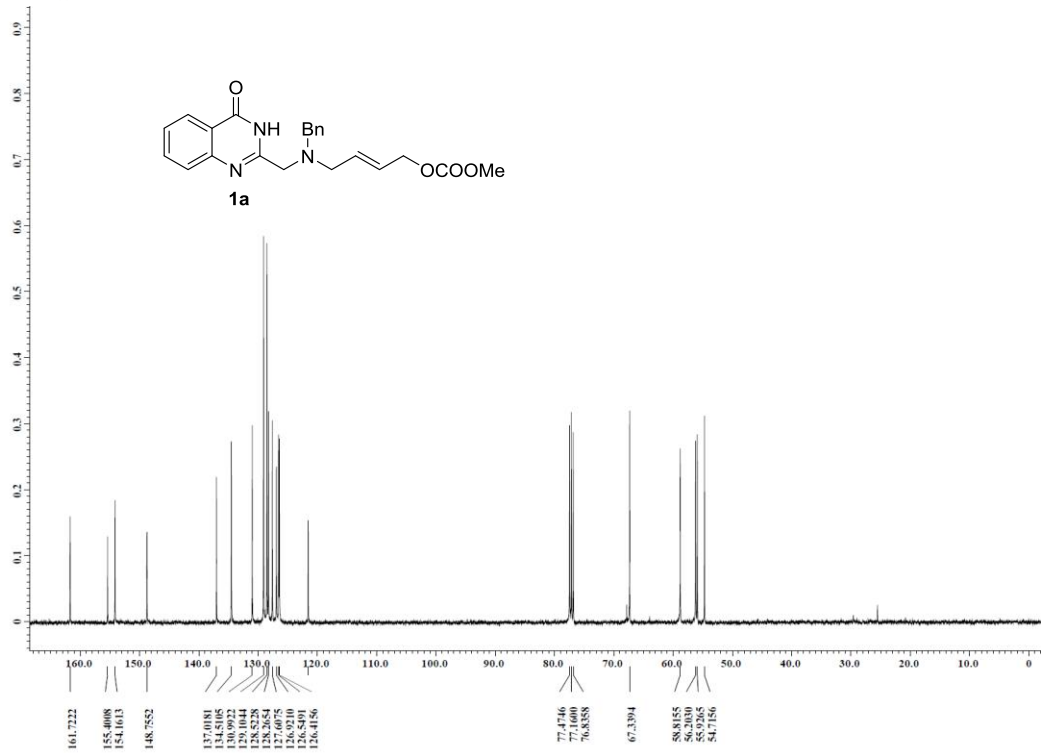
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.744	VB	0.6404	1779.53870	41.70943	50.4865
2	14.451	BB	0.9196	1745.24316	27.93467	49.5135

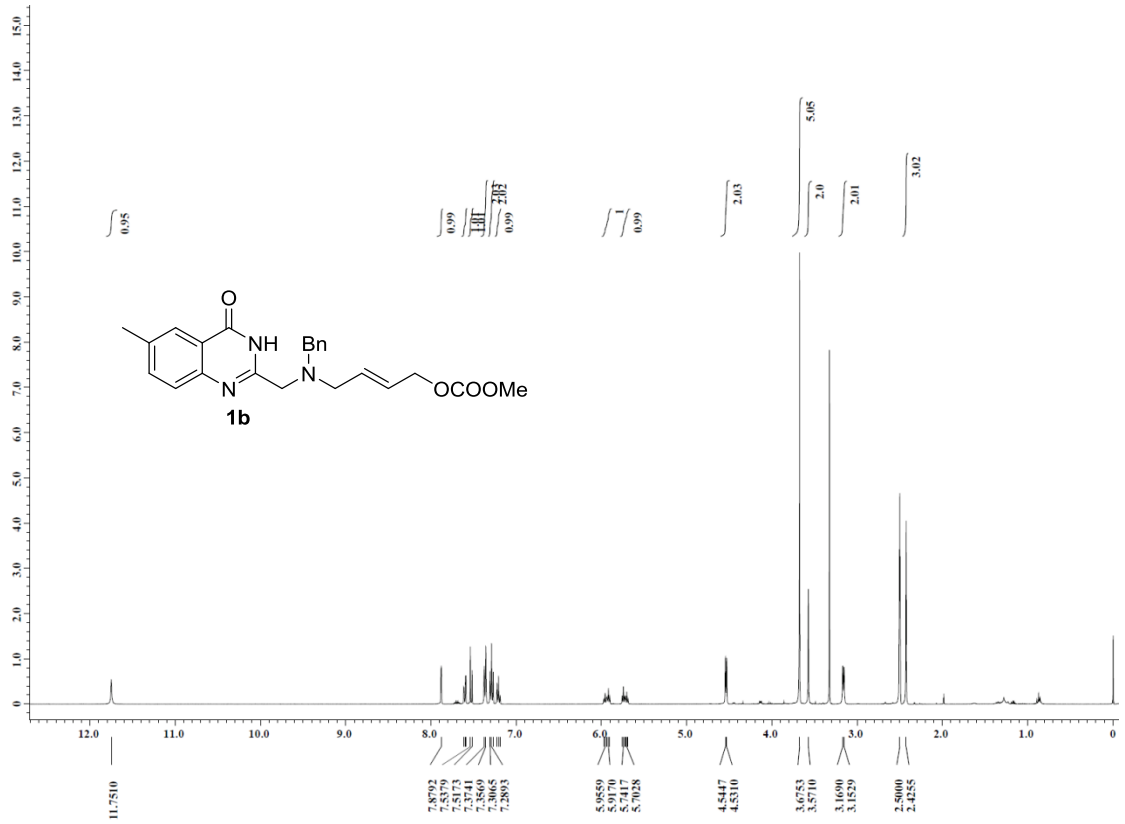


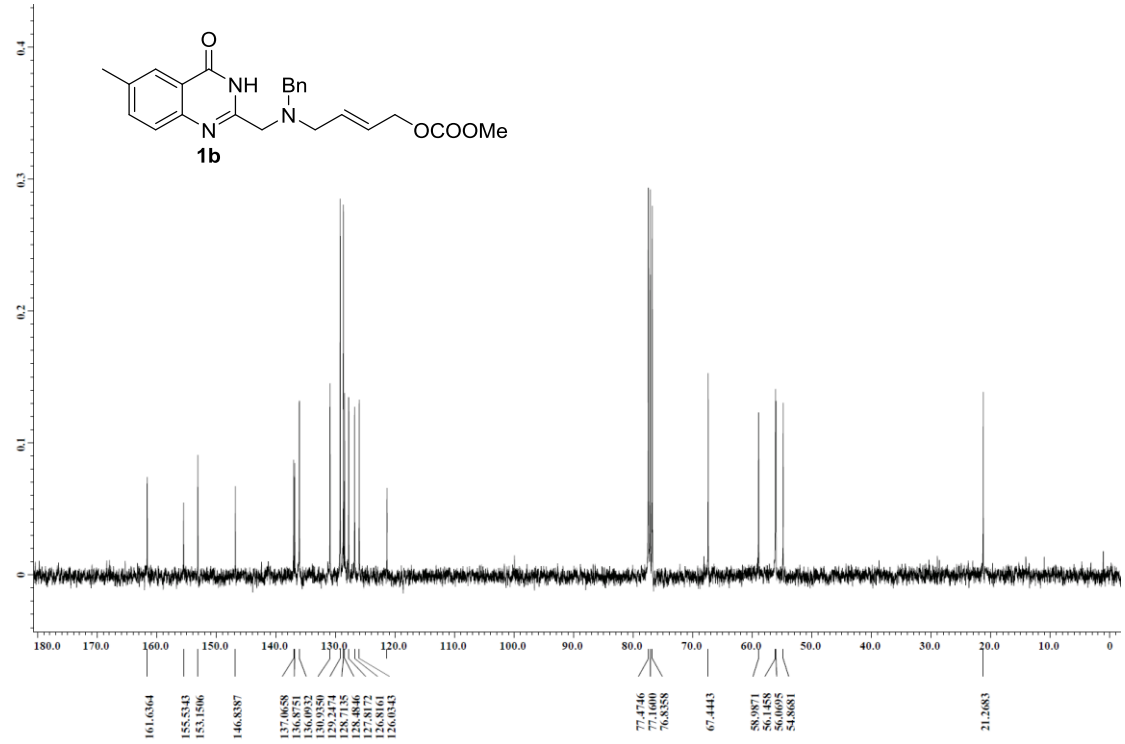
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.546	VB	0.6015	205.41023	4.92565	2.4247
2	13.664	MM	0.9711	8266.14648	141.86929	97.5753

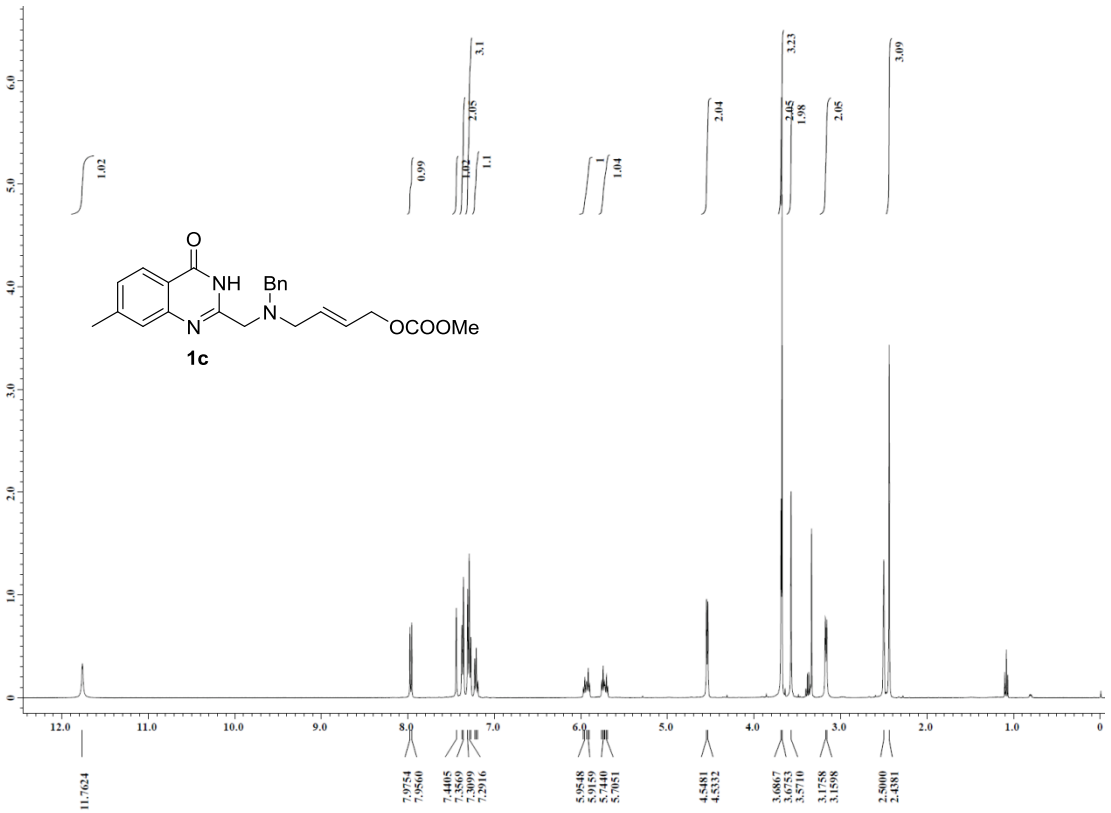
10. NMR Spectra of 1a-1w, 2a-2w, 3 and 4

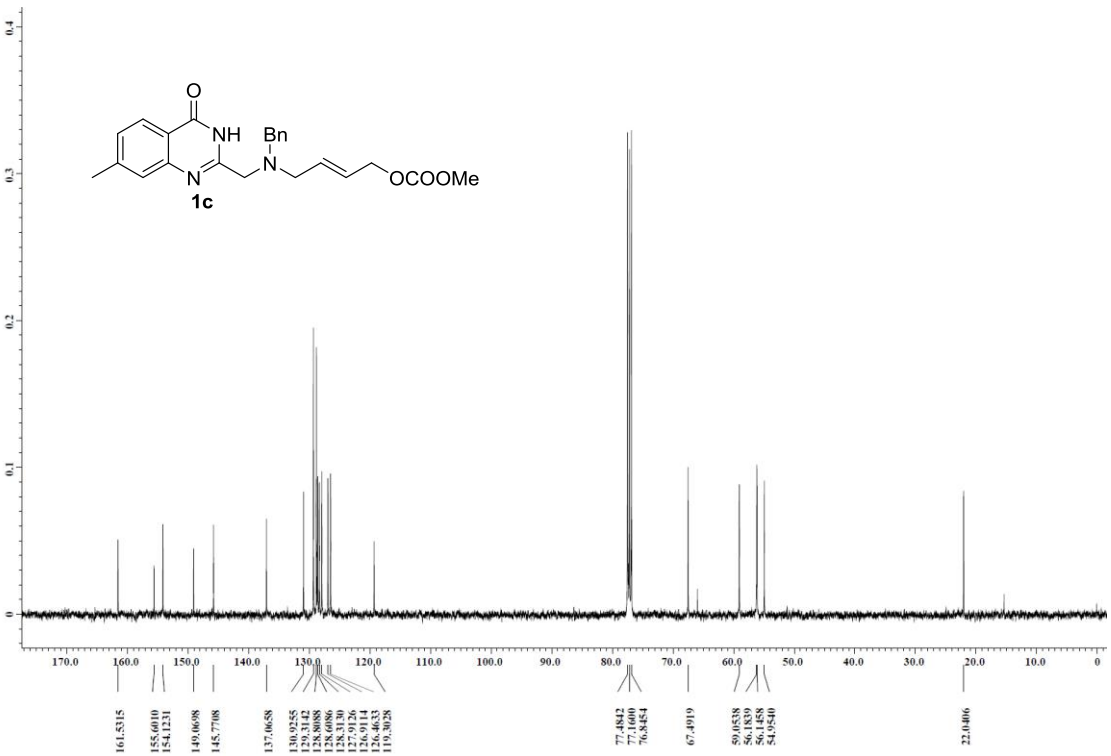


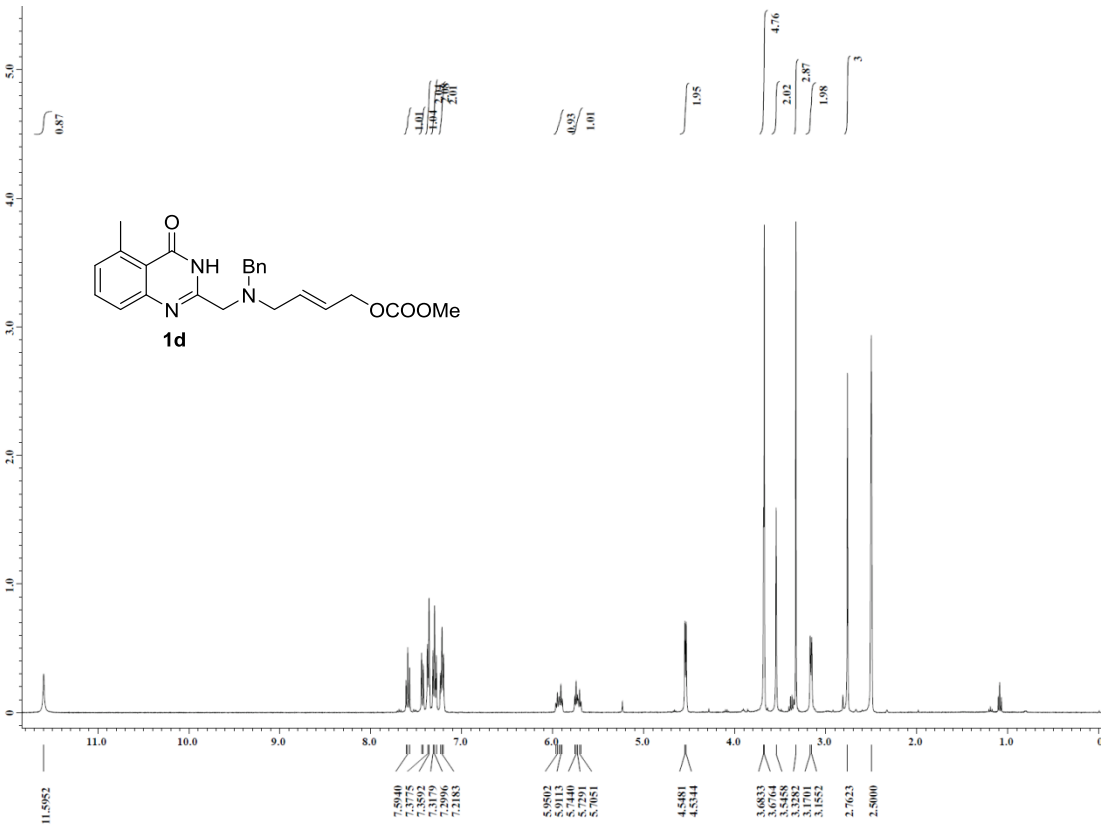


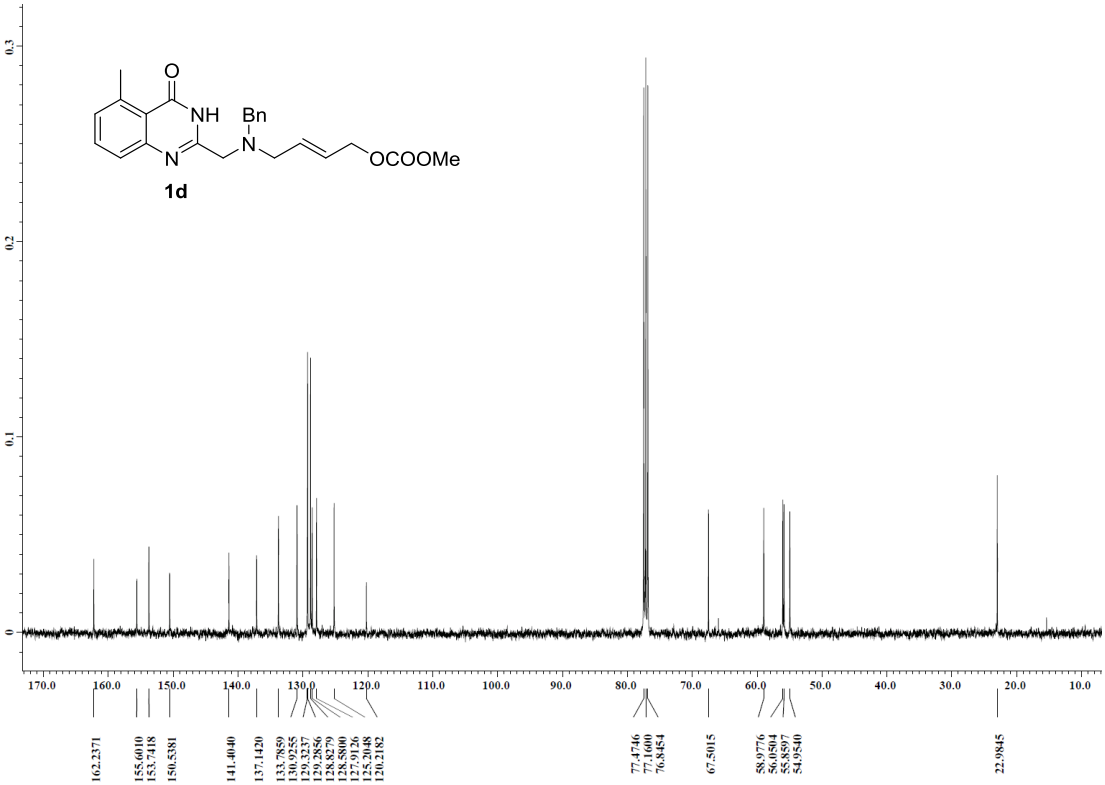

O
NH
Bn
N
N
OCOOMe
1b


O
NH
Bn
N
N
OCOOMe
1b


O
NH
Bn
N
N
OCOOMe
1c


O
NH
Bn
N
N
OCOOMe
1c


O
NH
Bn
N
N
OCOOMe
1d


O
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Bn
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N
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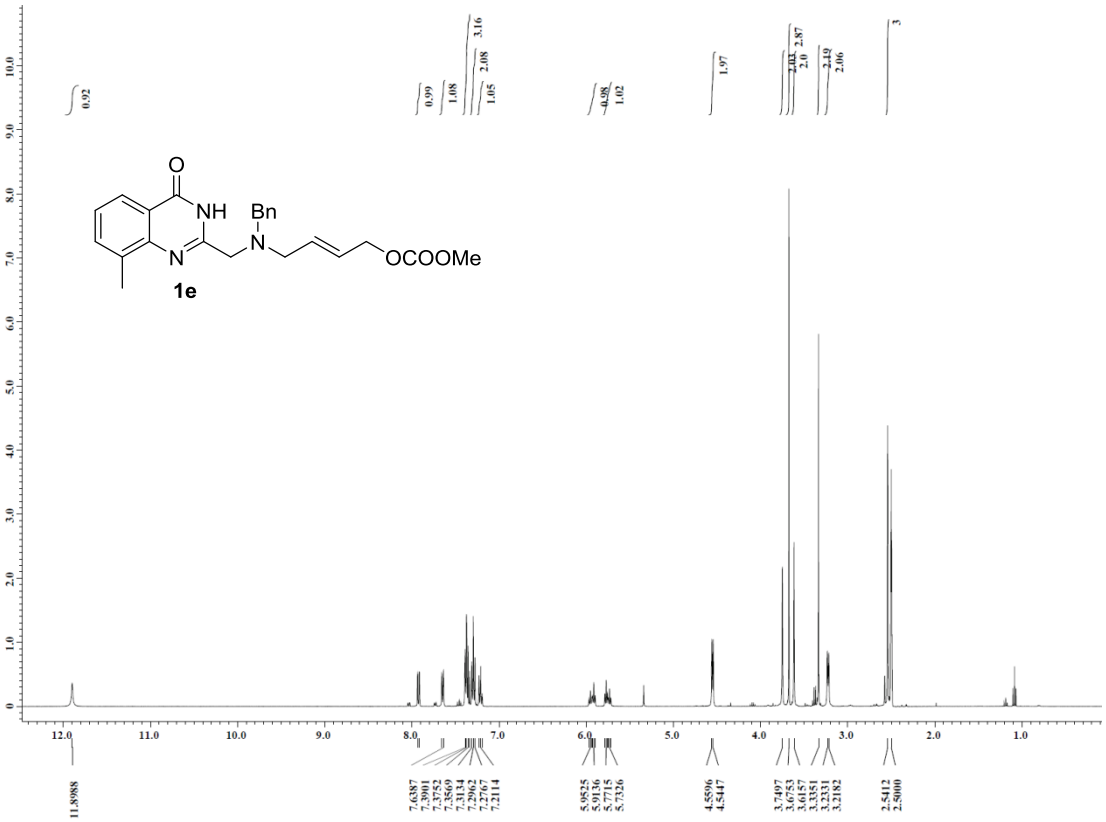
1d


O
NH
Bn
N
N
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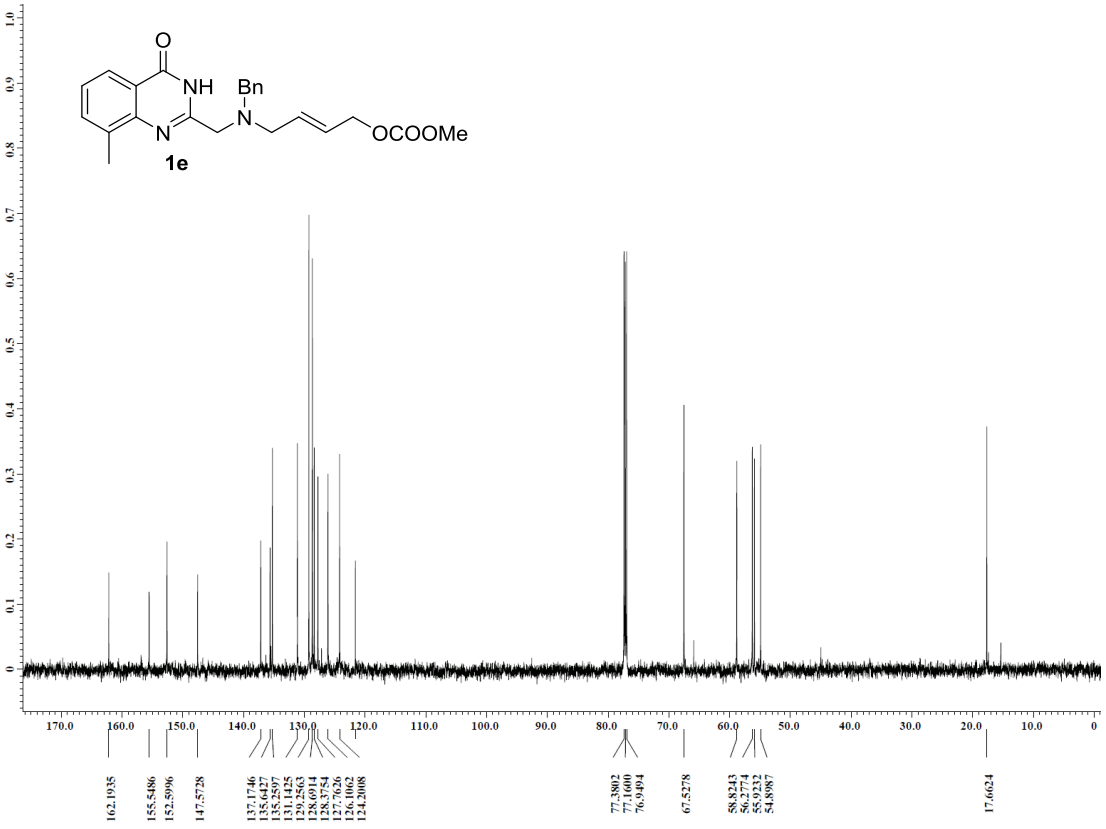
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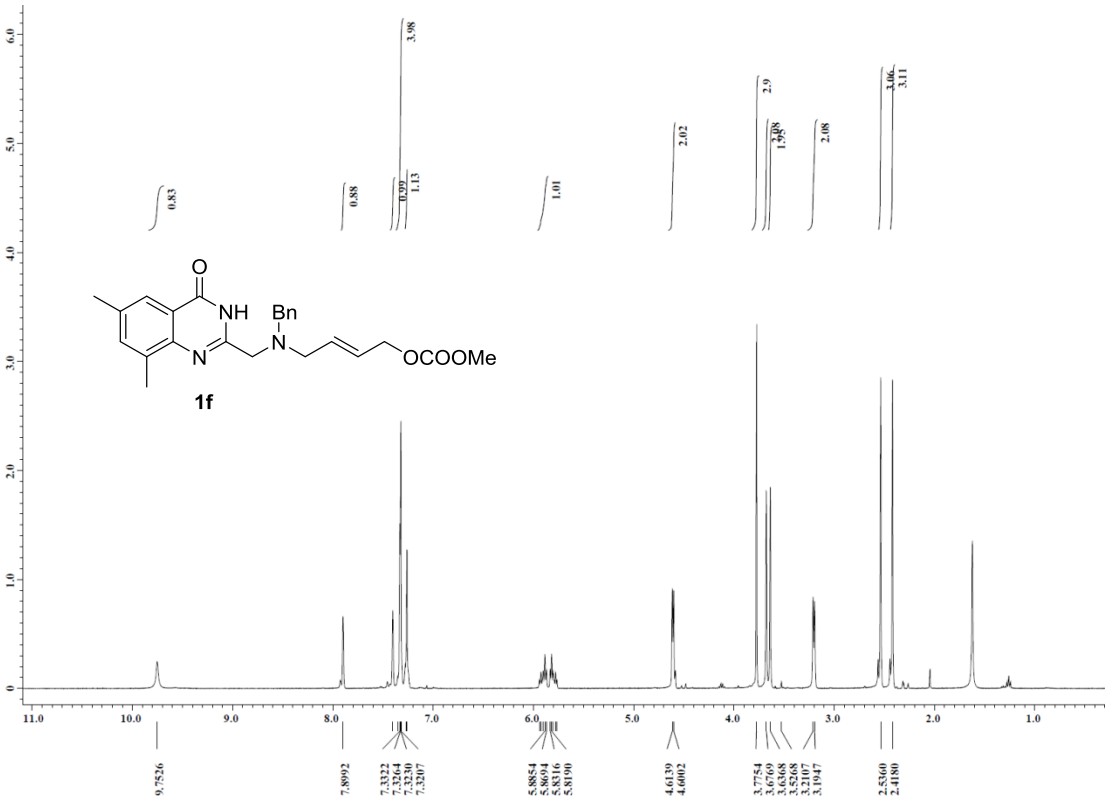
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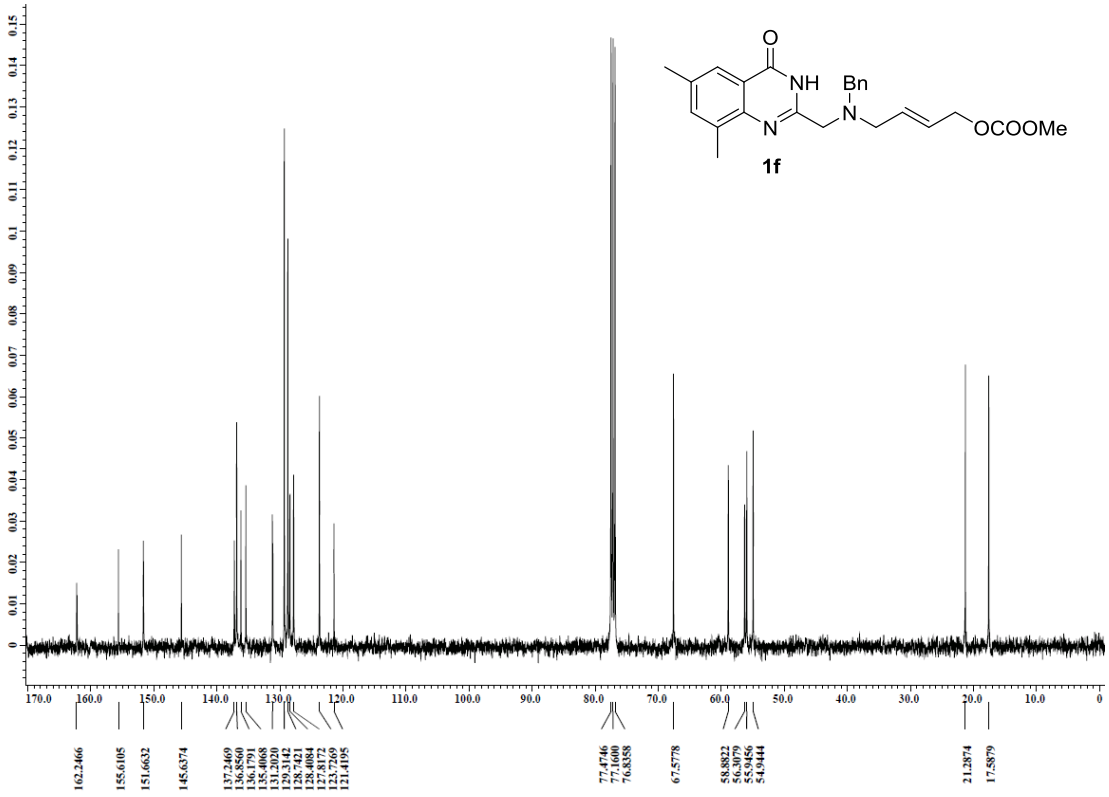
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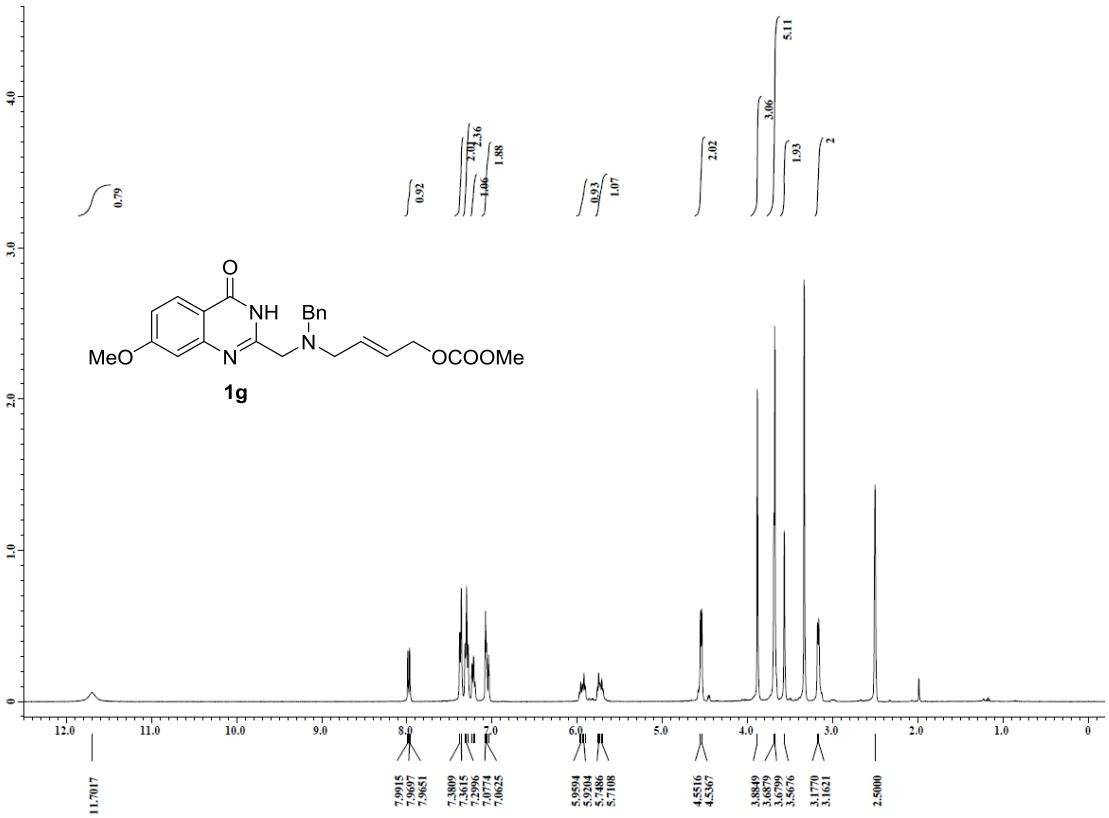
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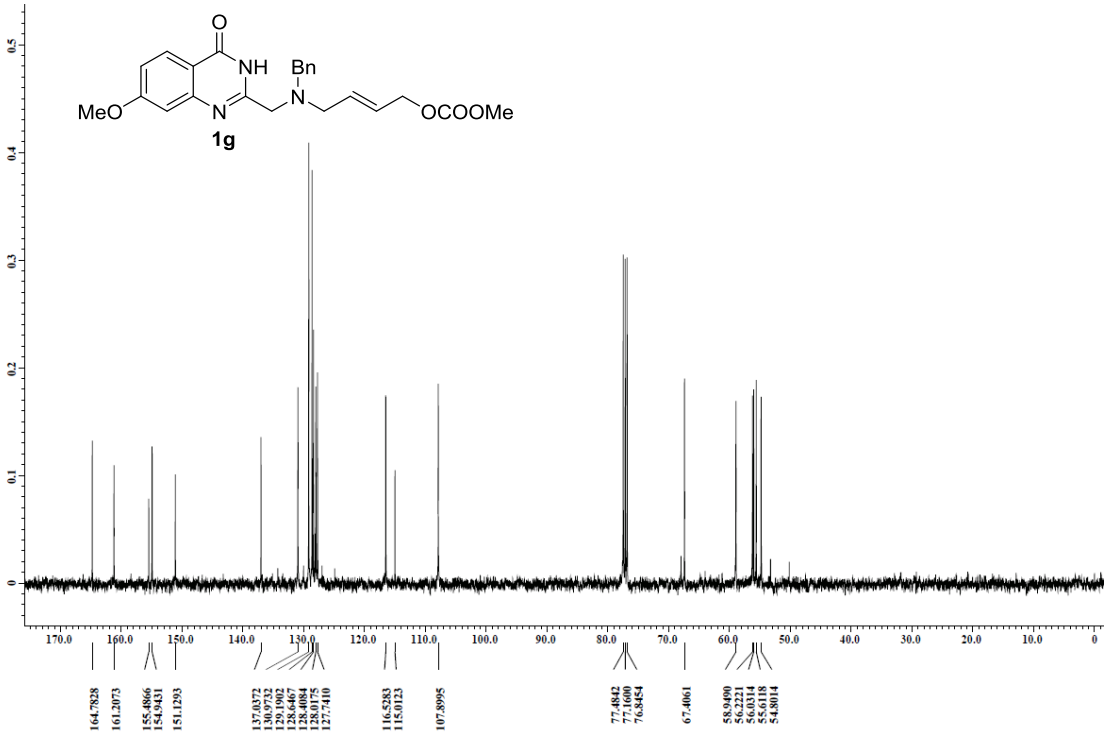
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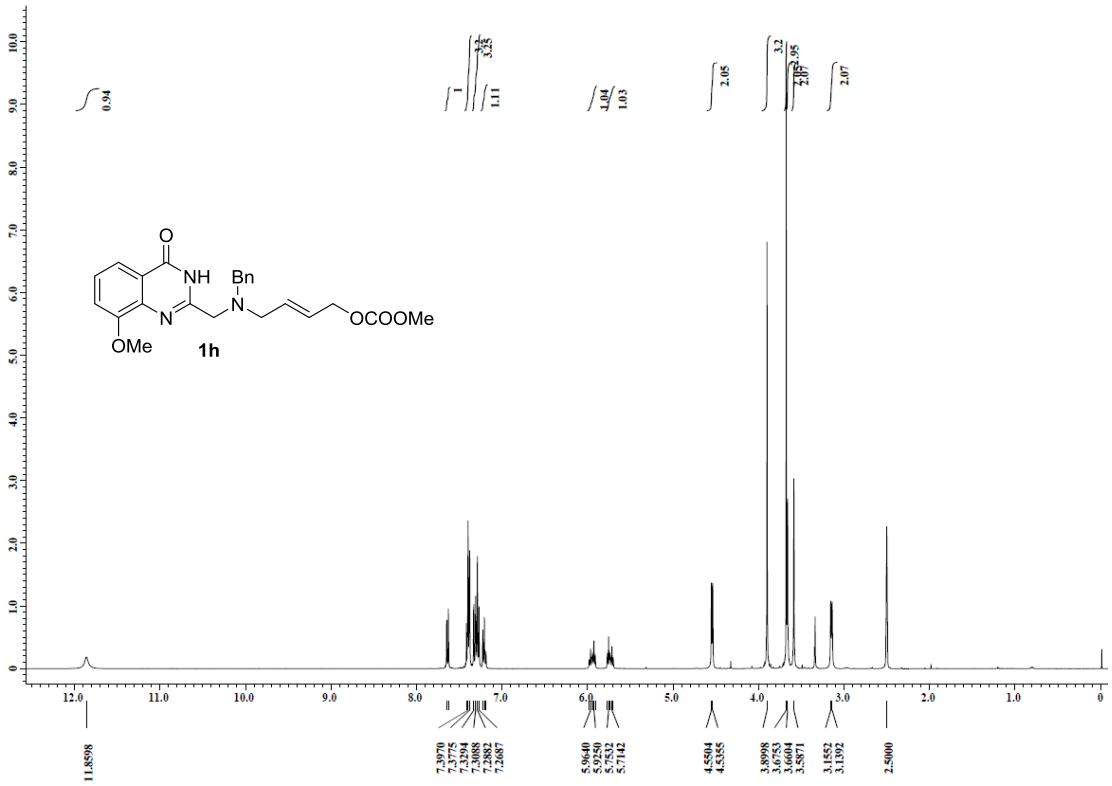
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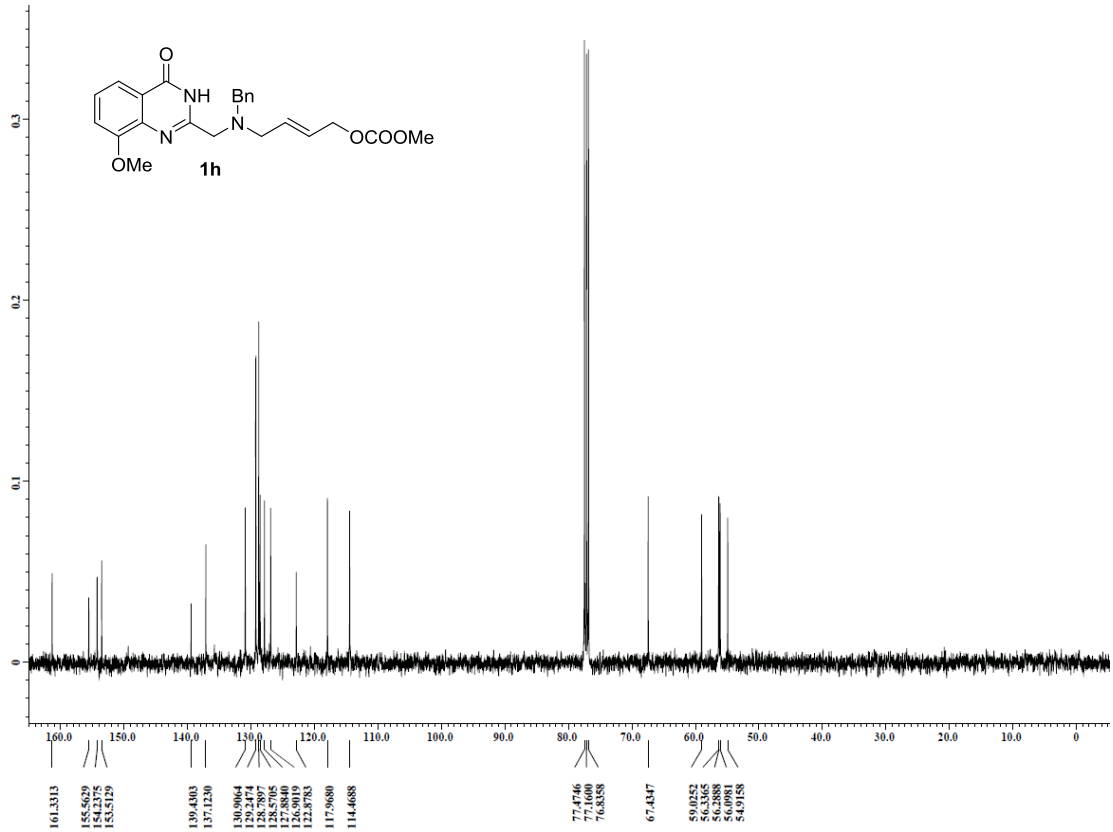
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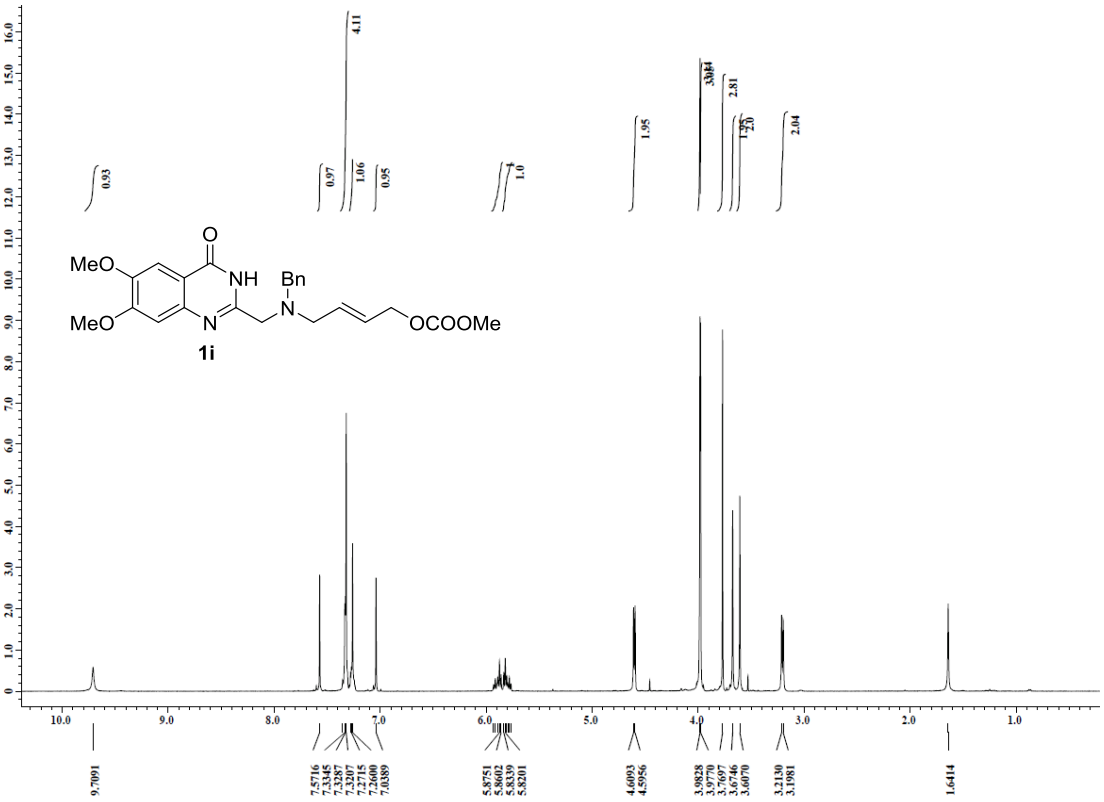
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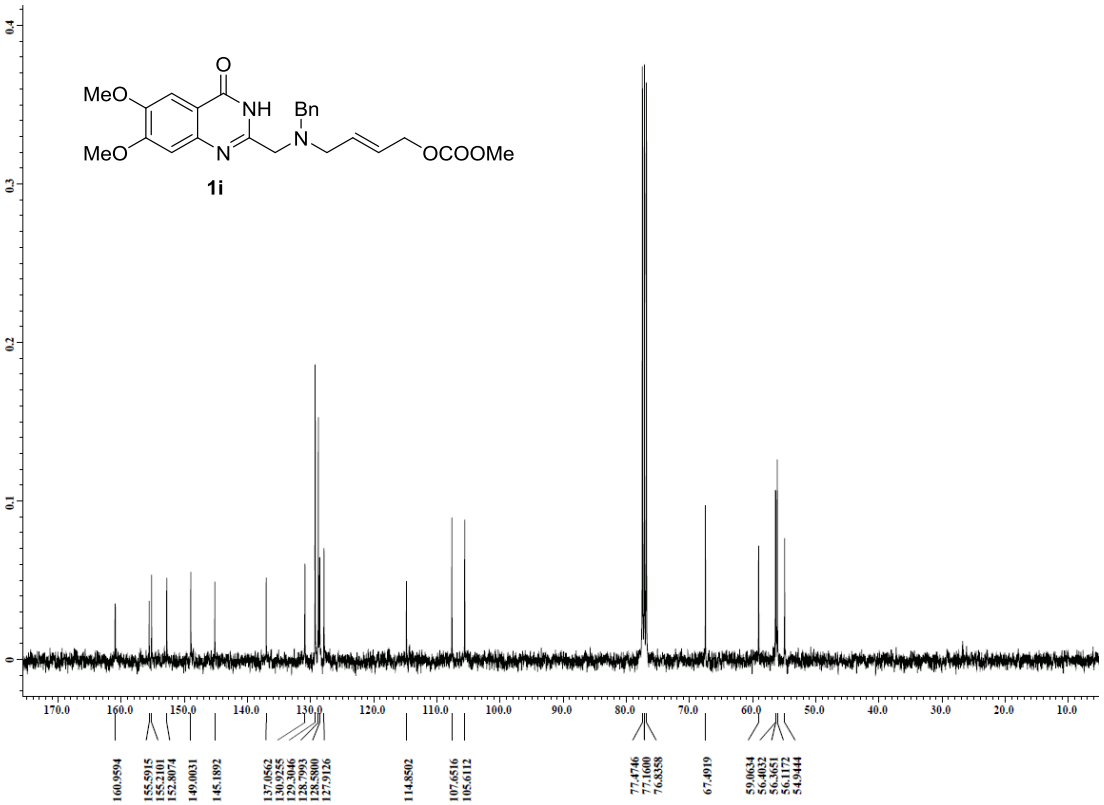
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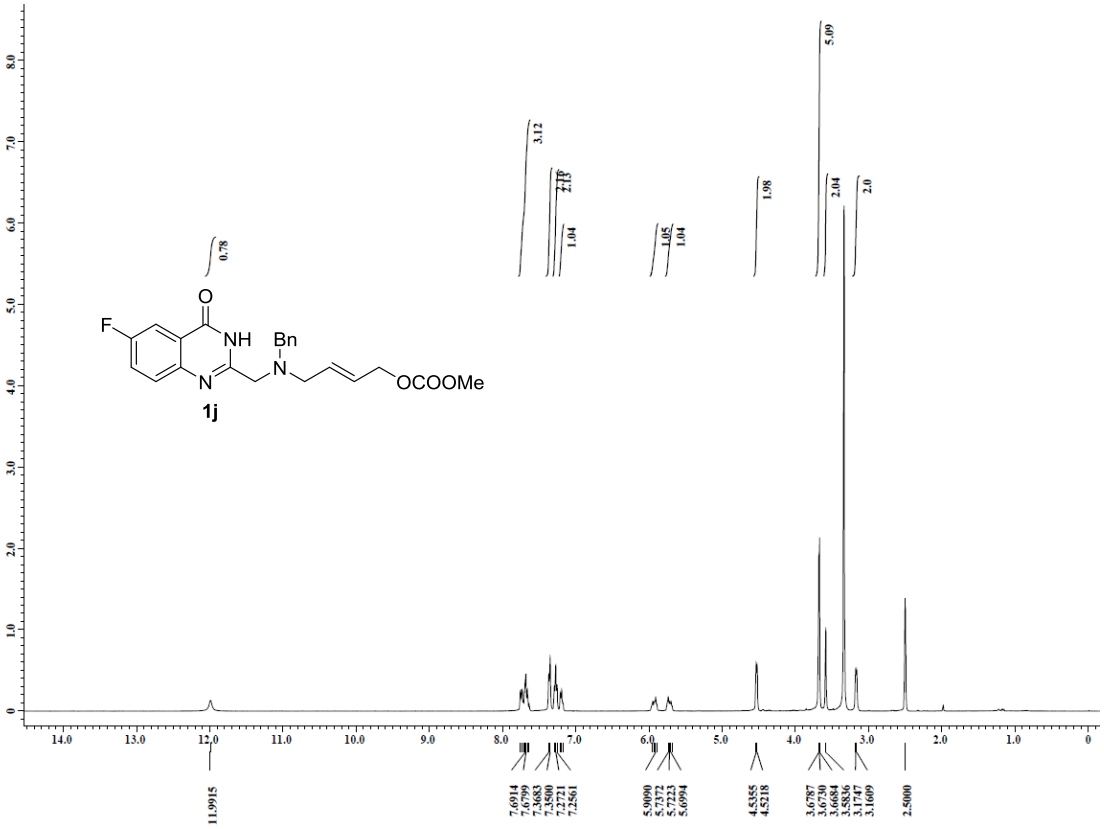
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2.04
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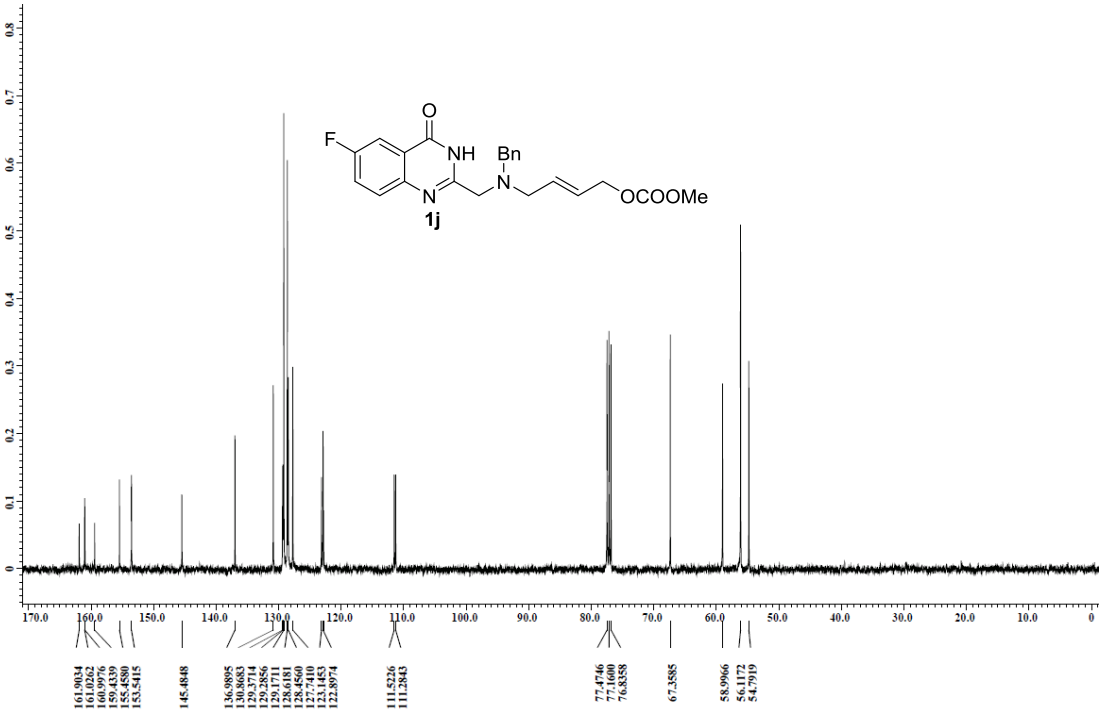
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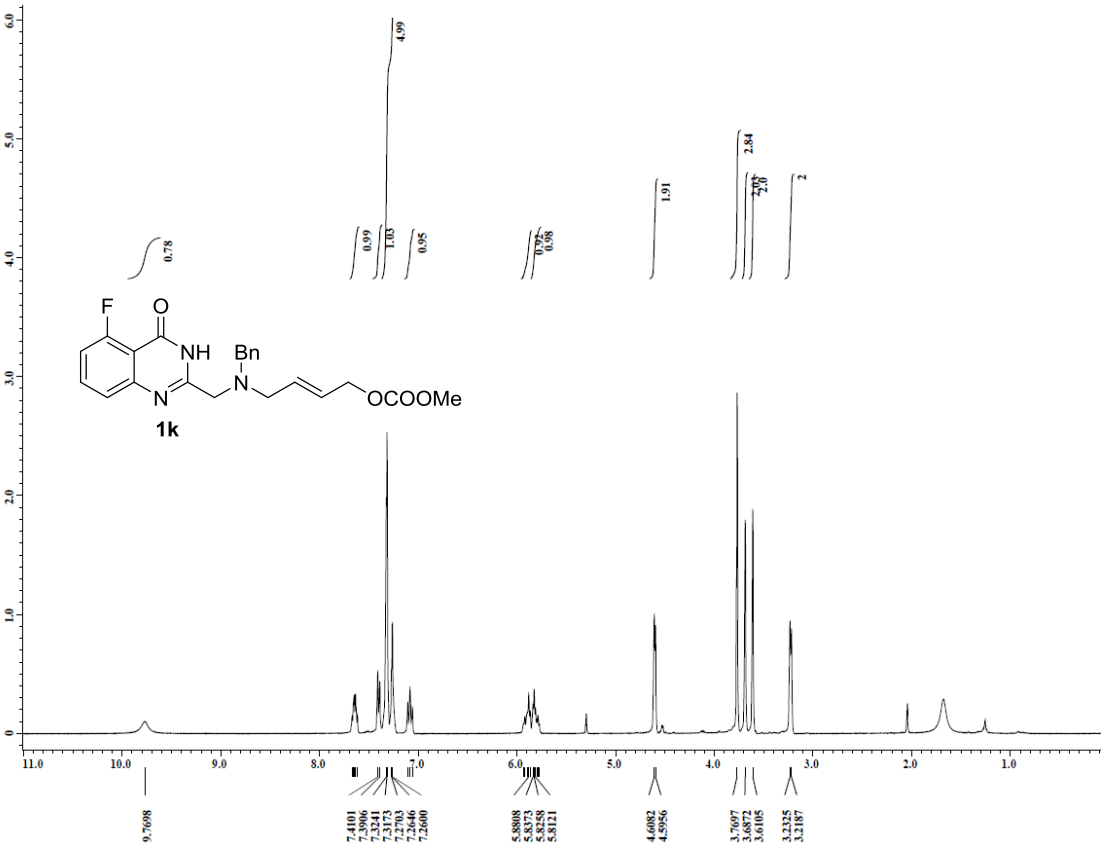
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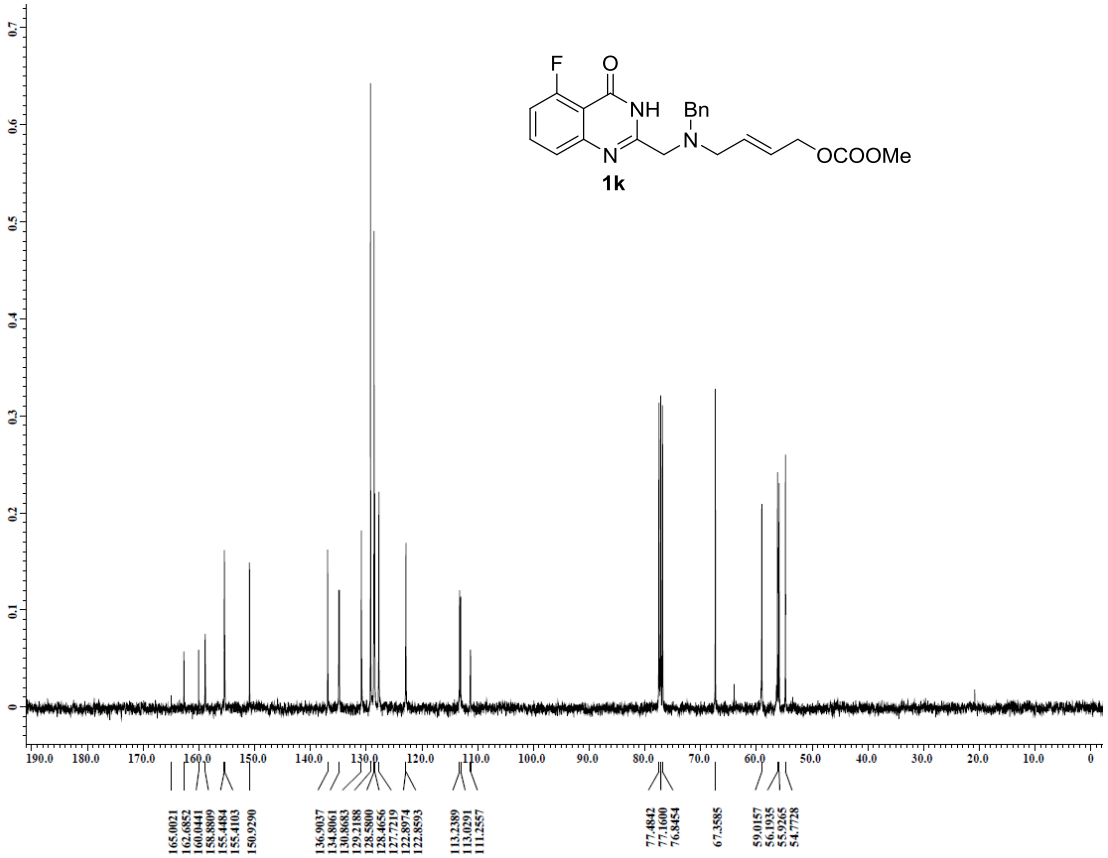
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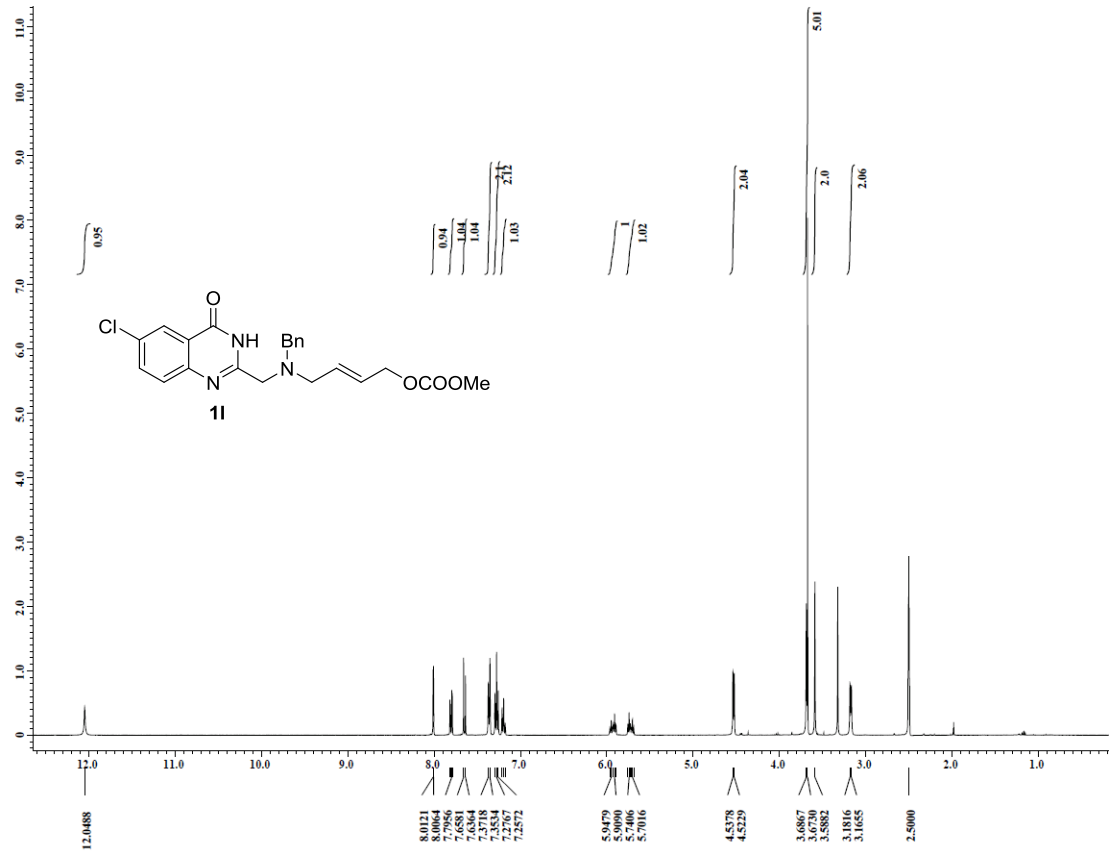
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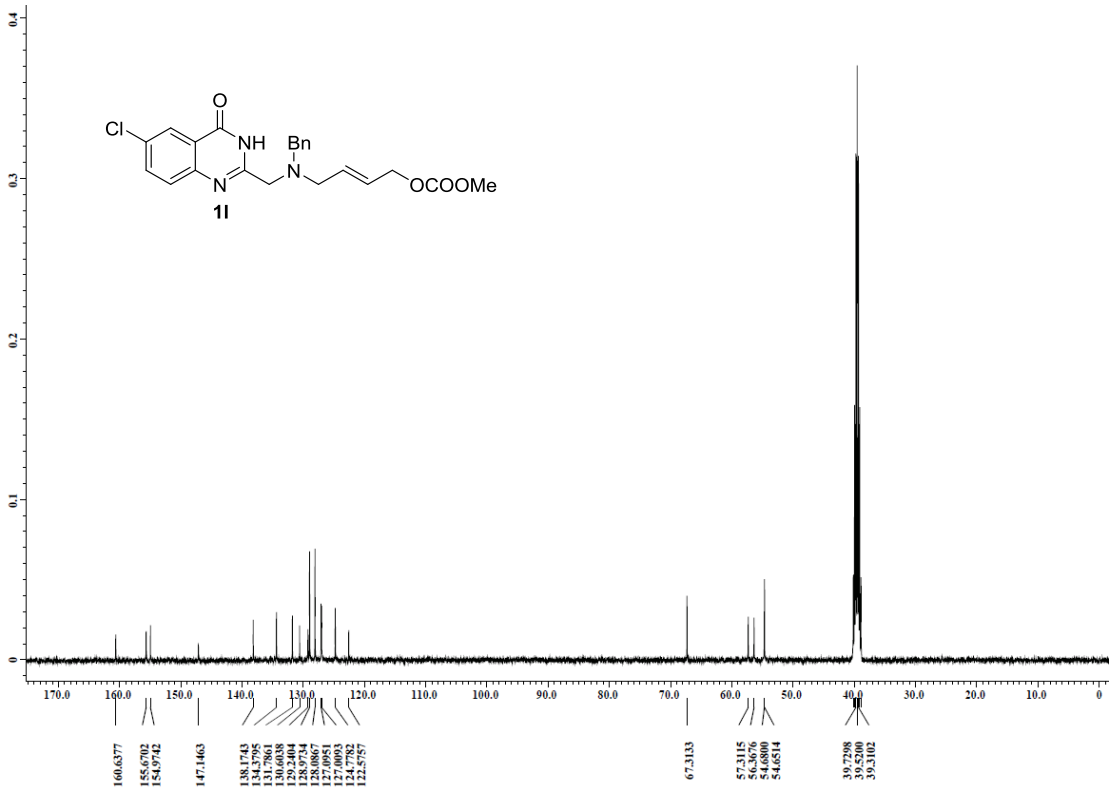
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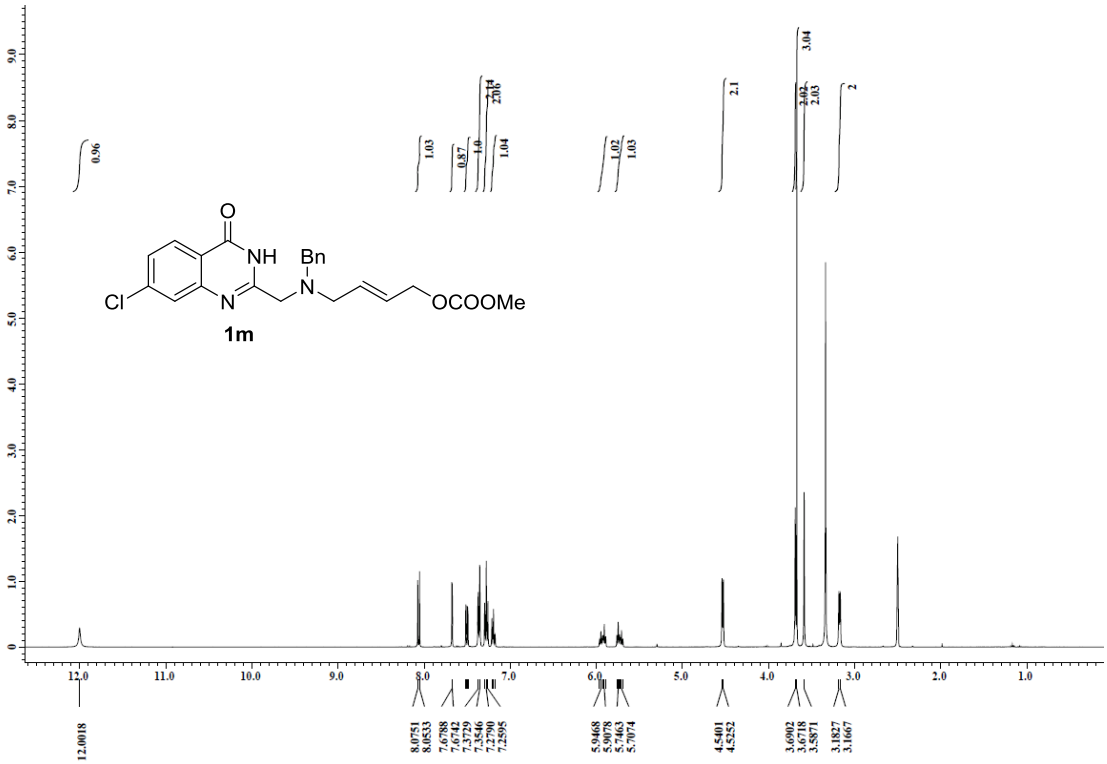
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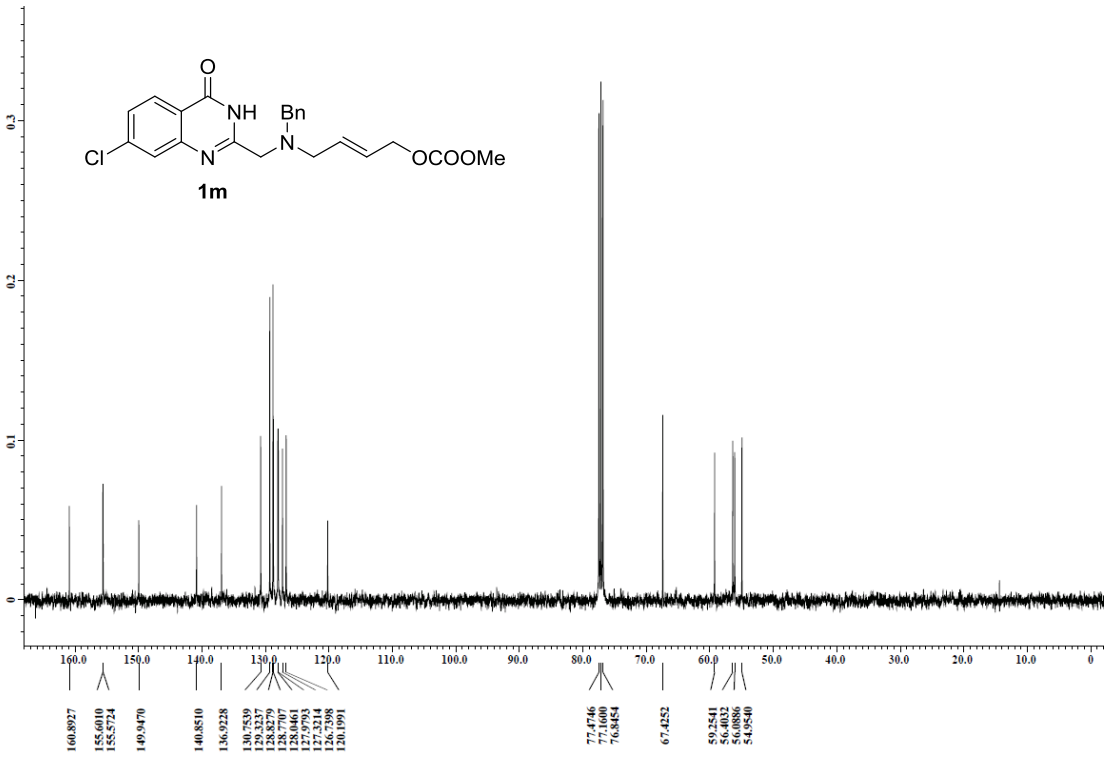
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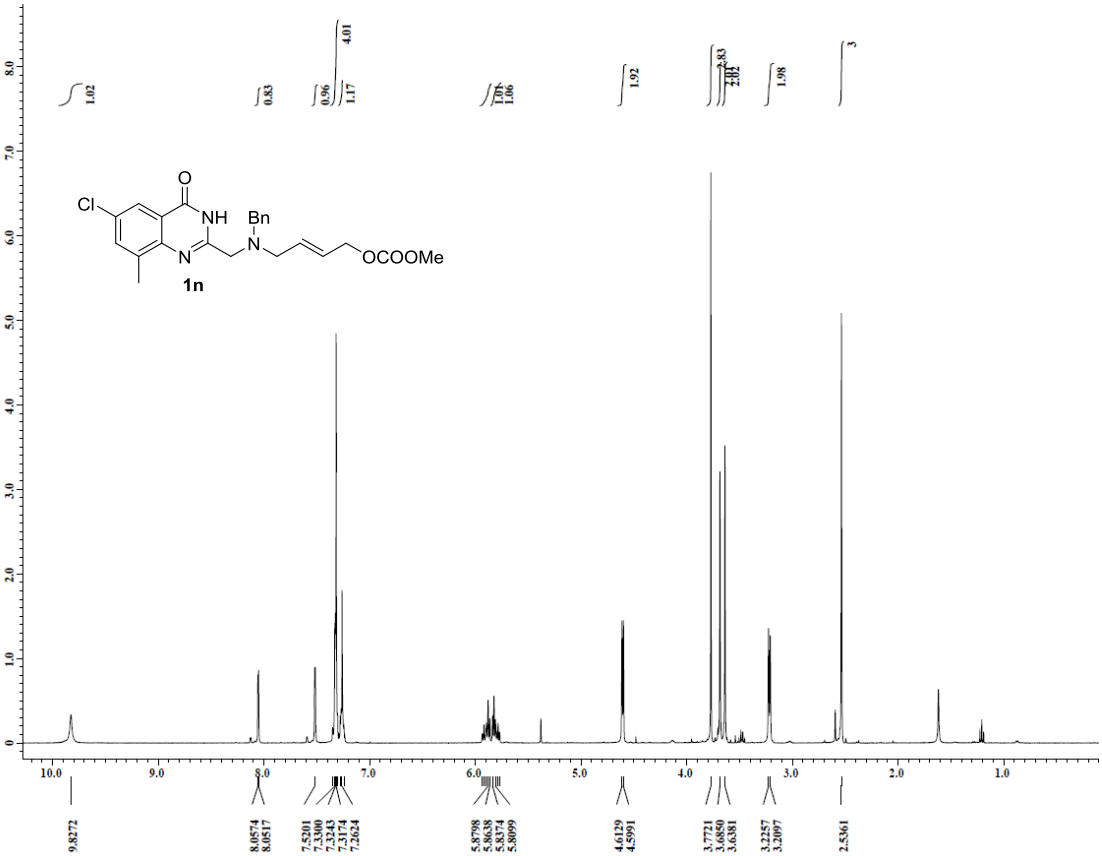
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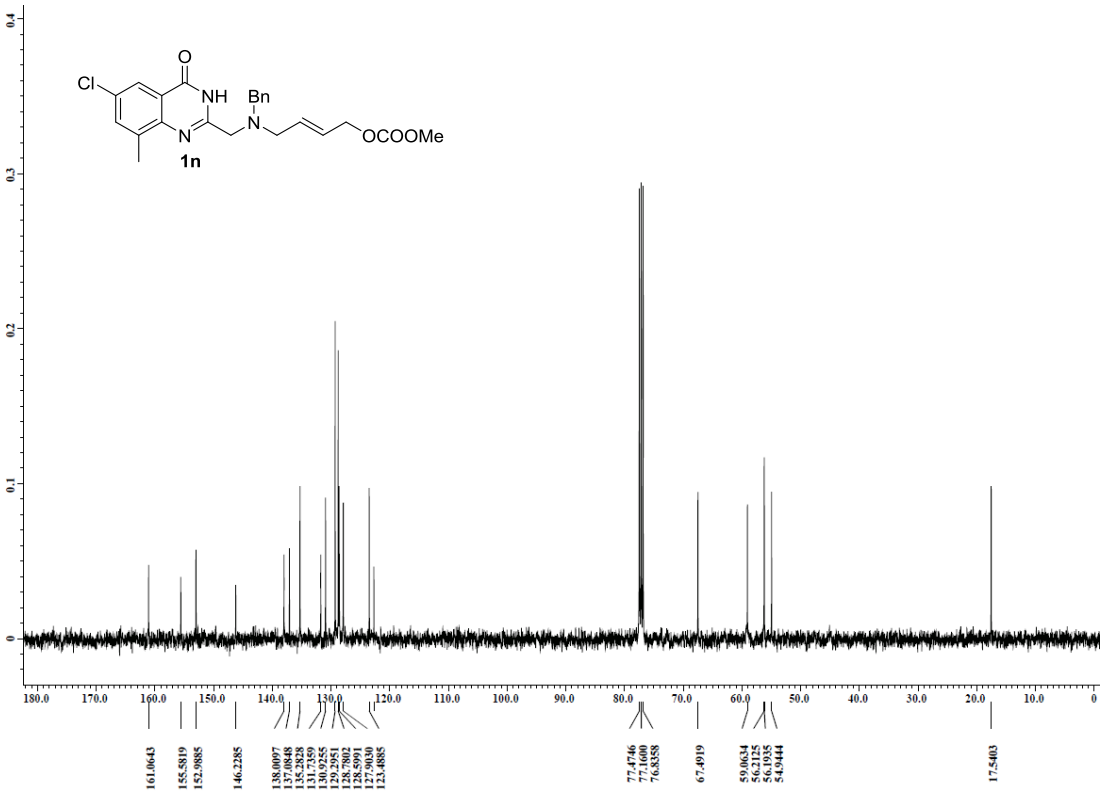
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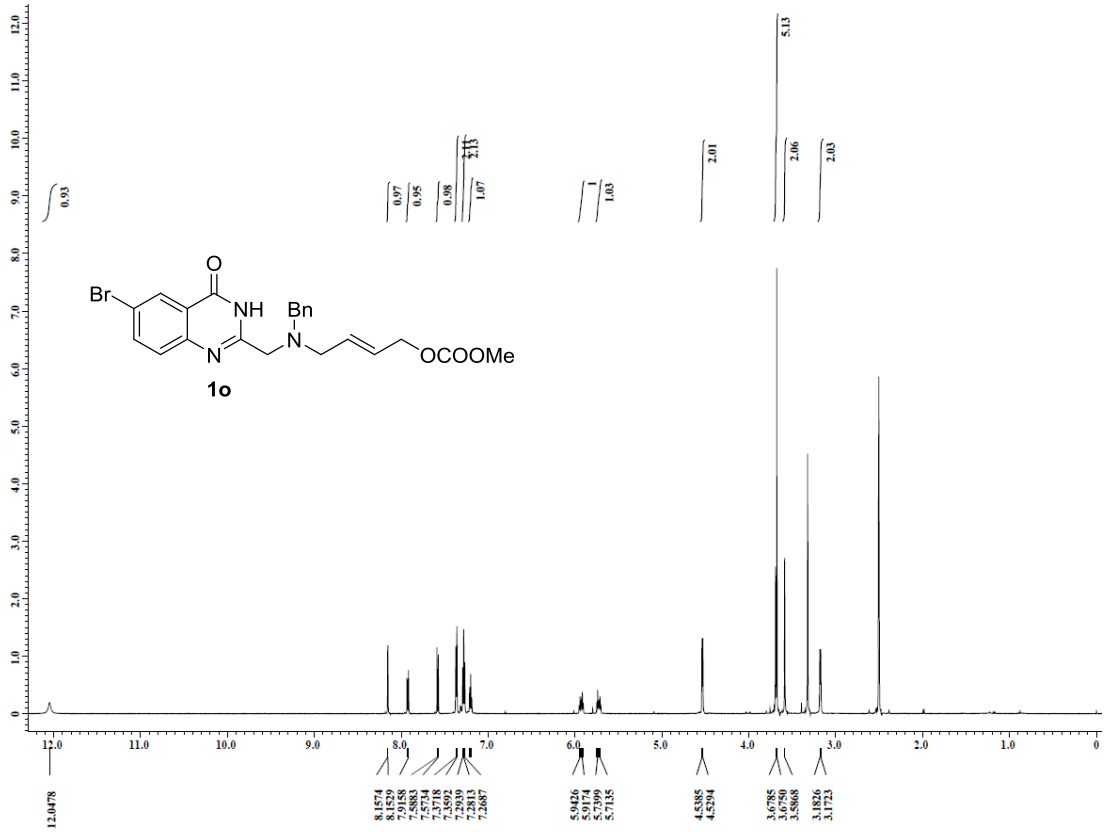
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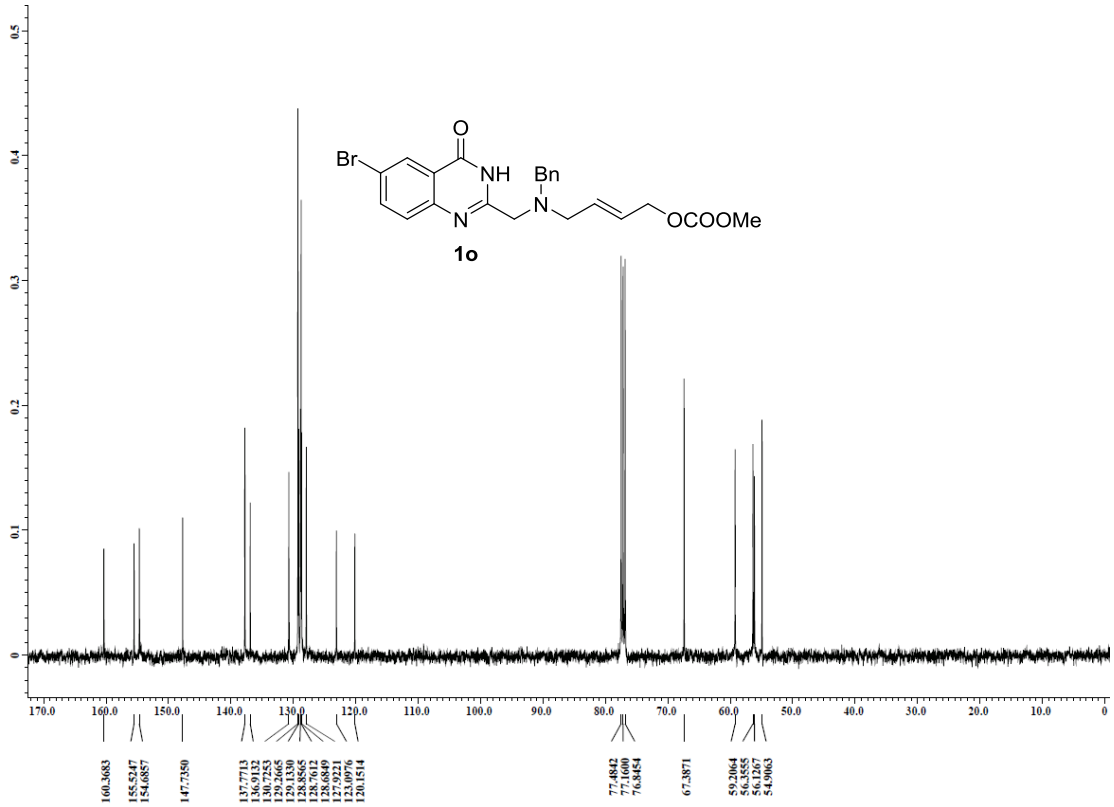
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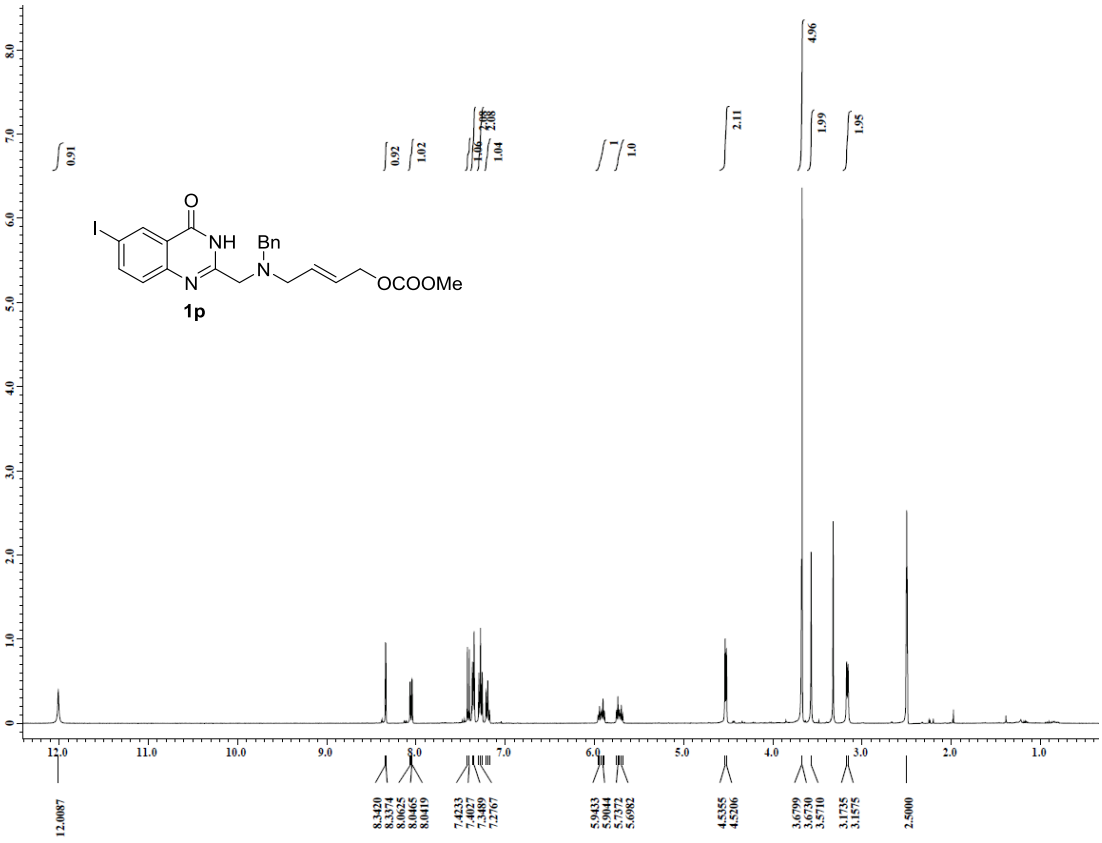
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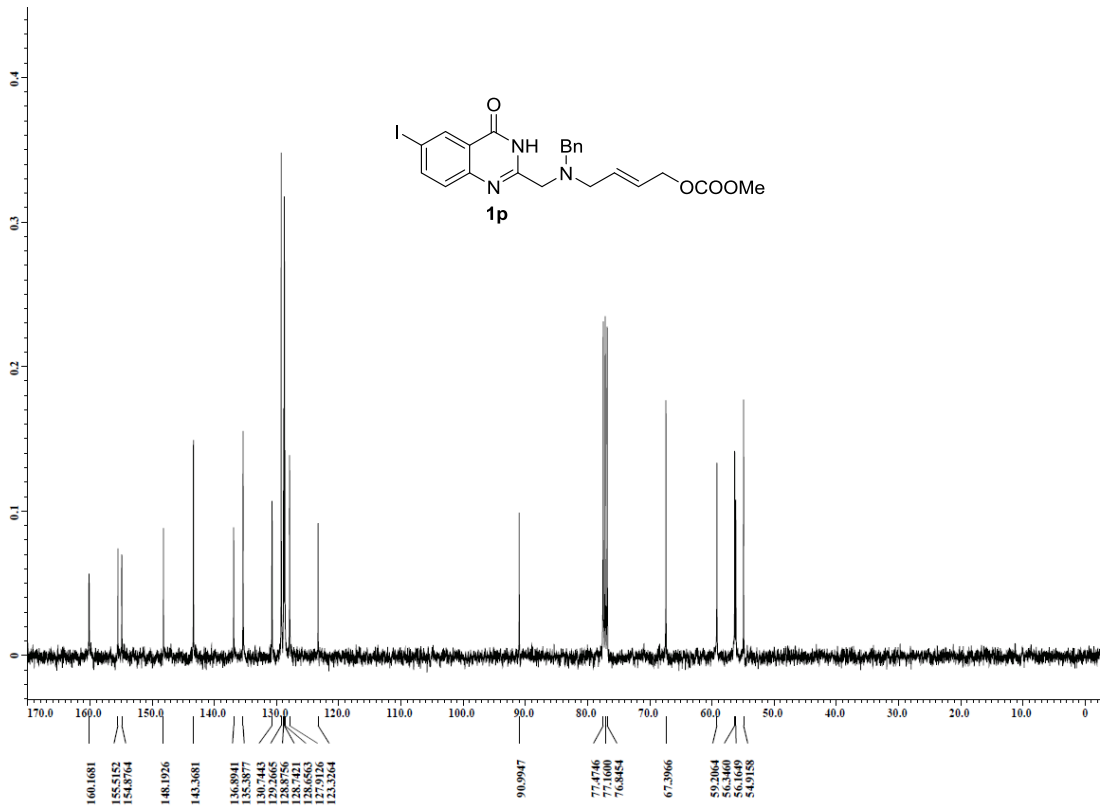
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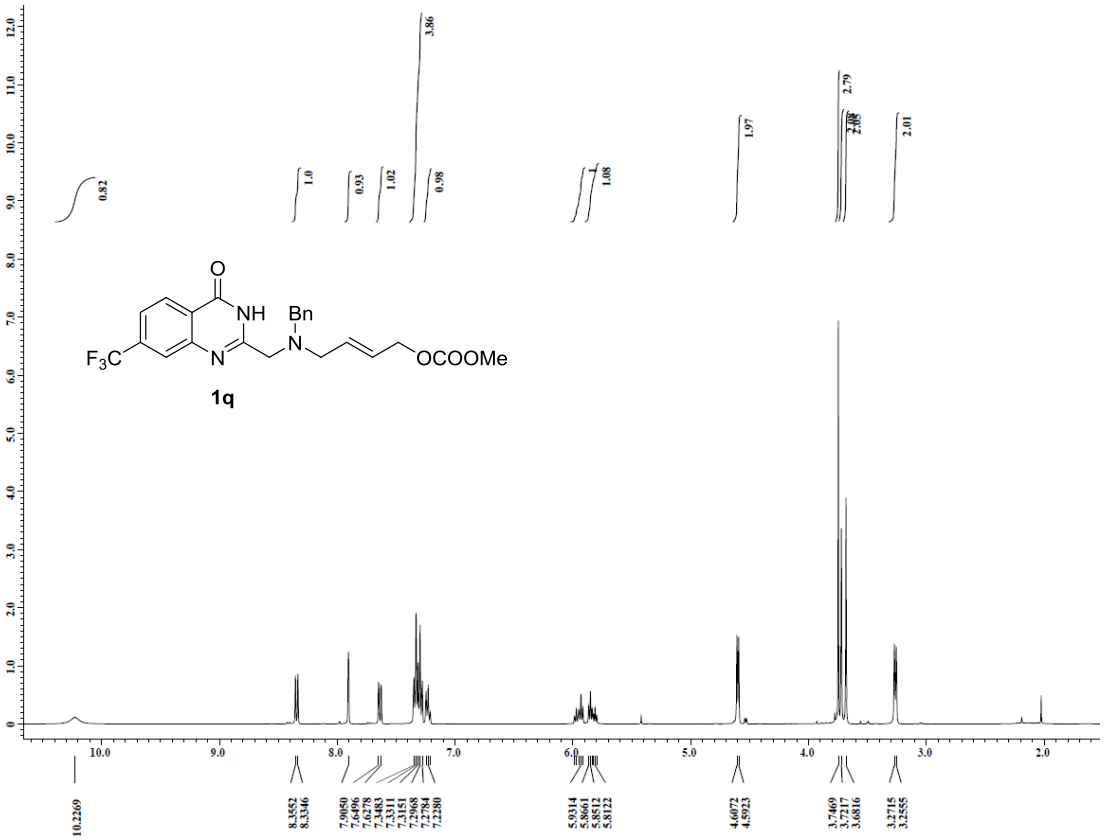
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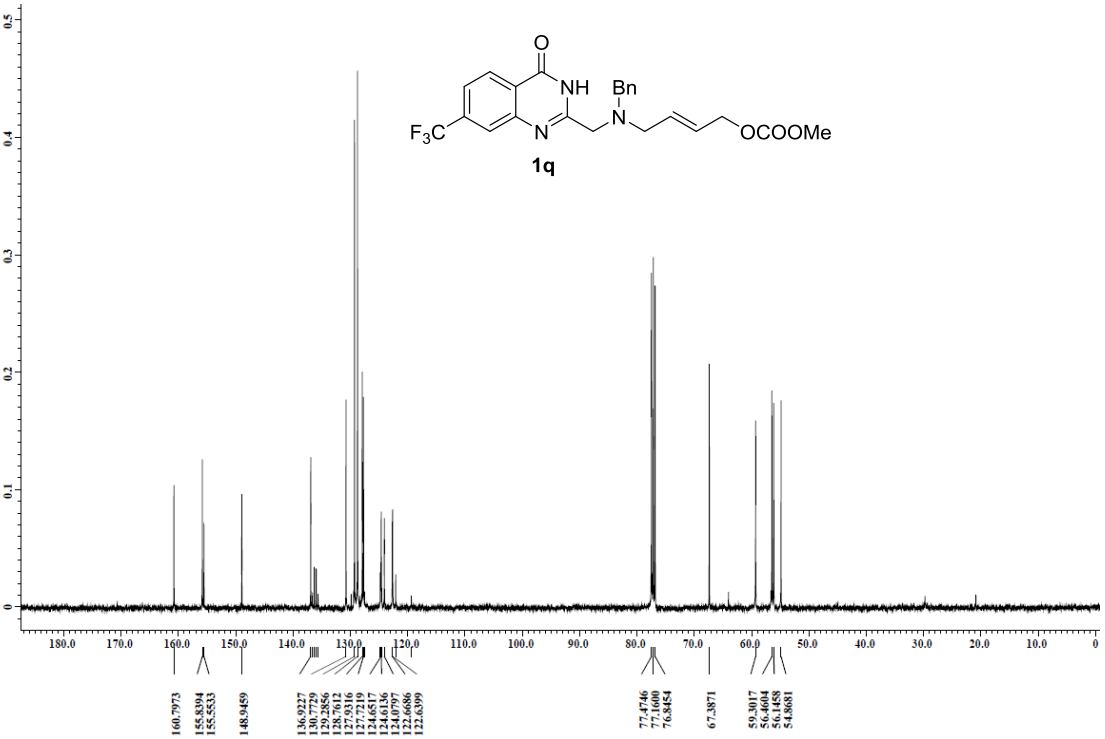
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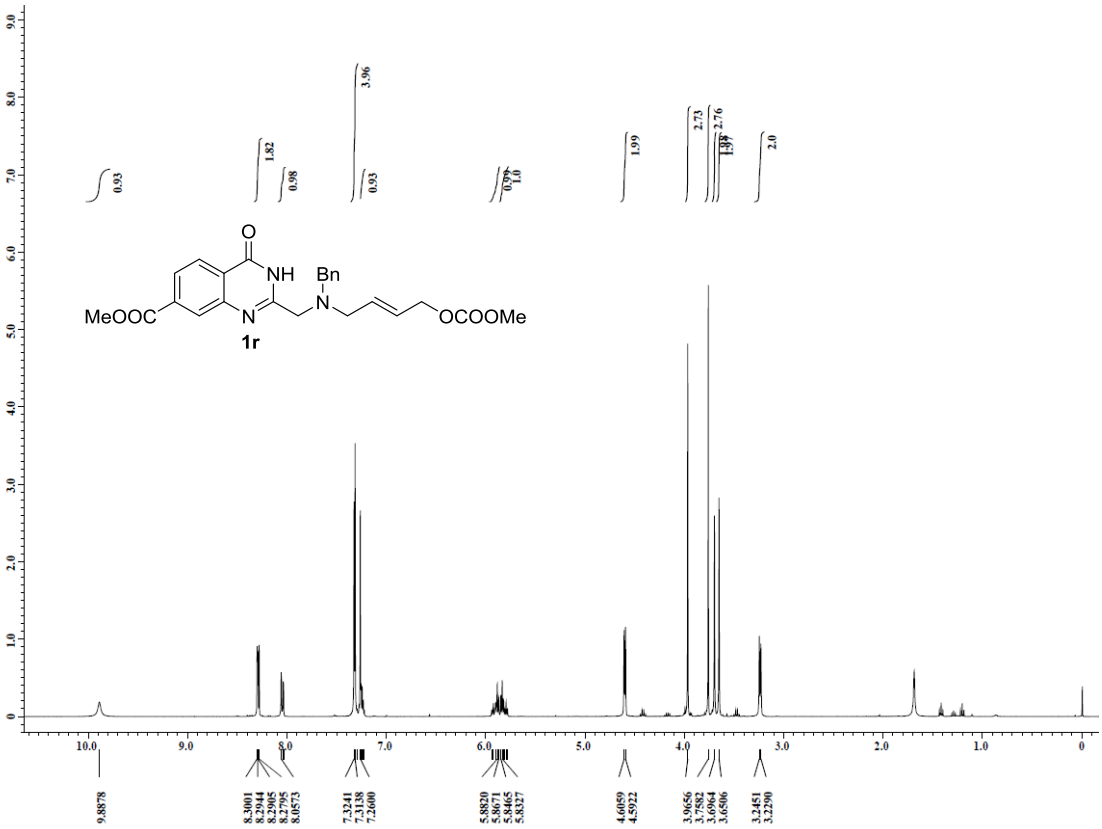
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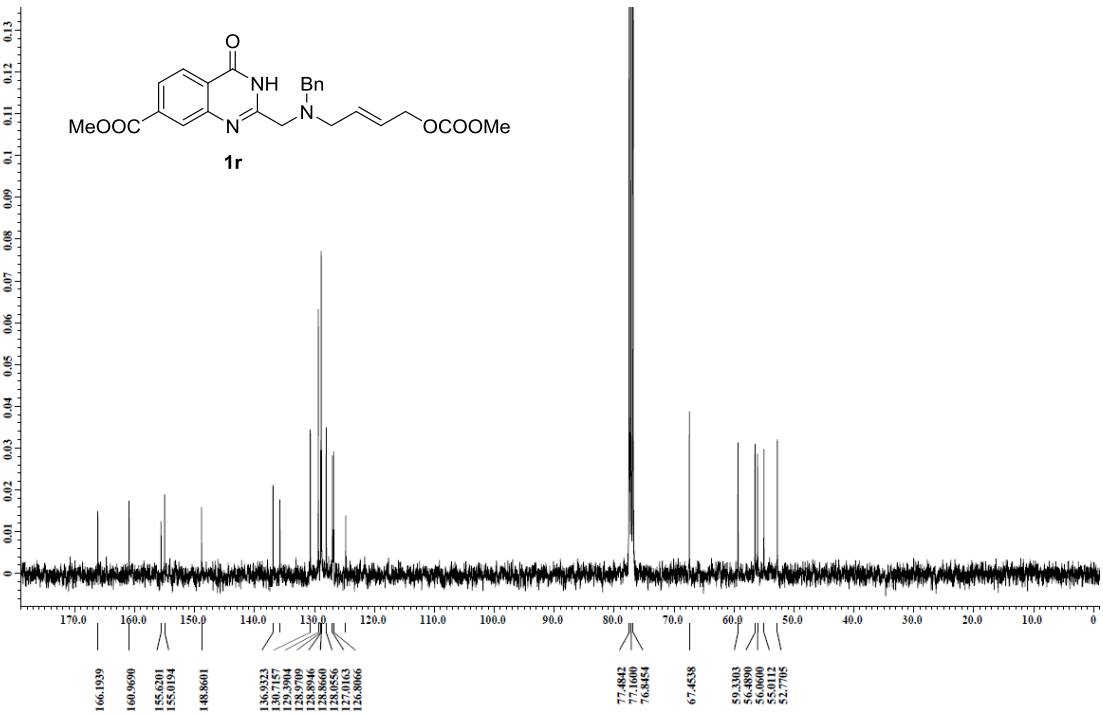
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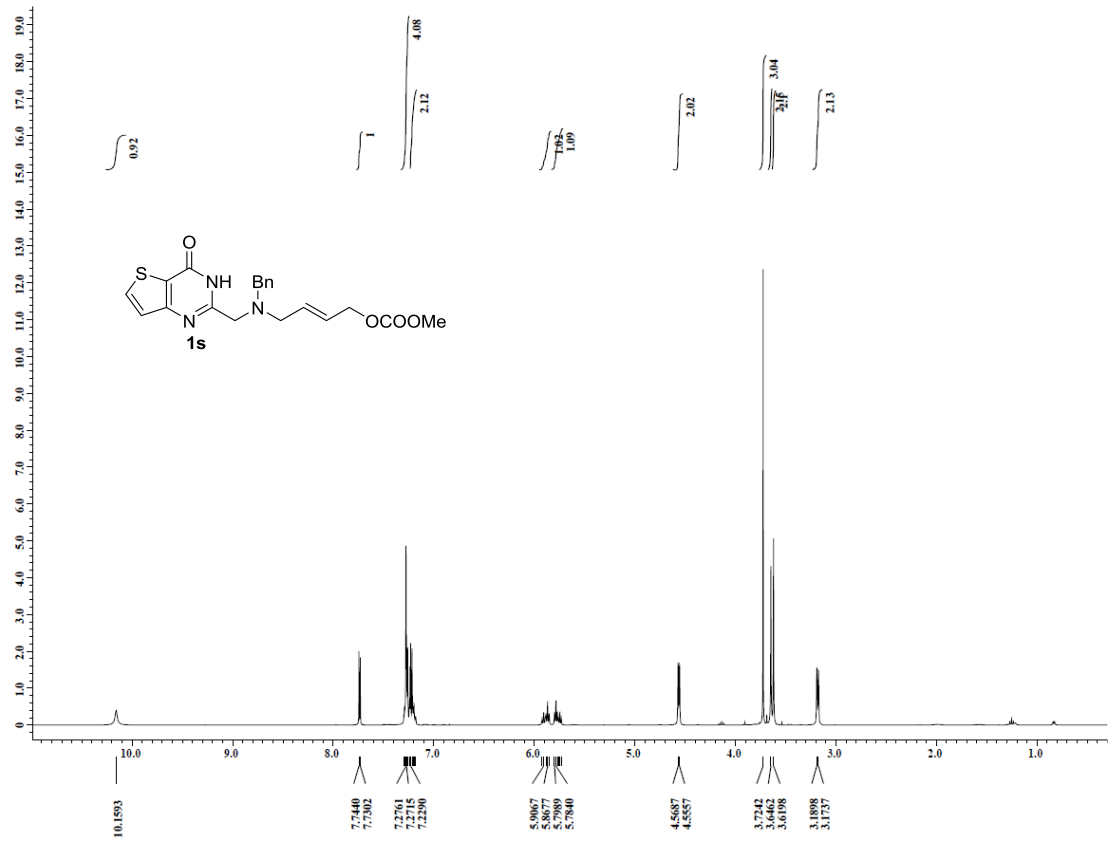
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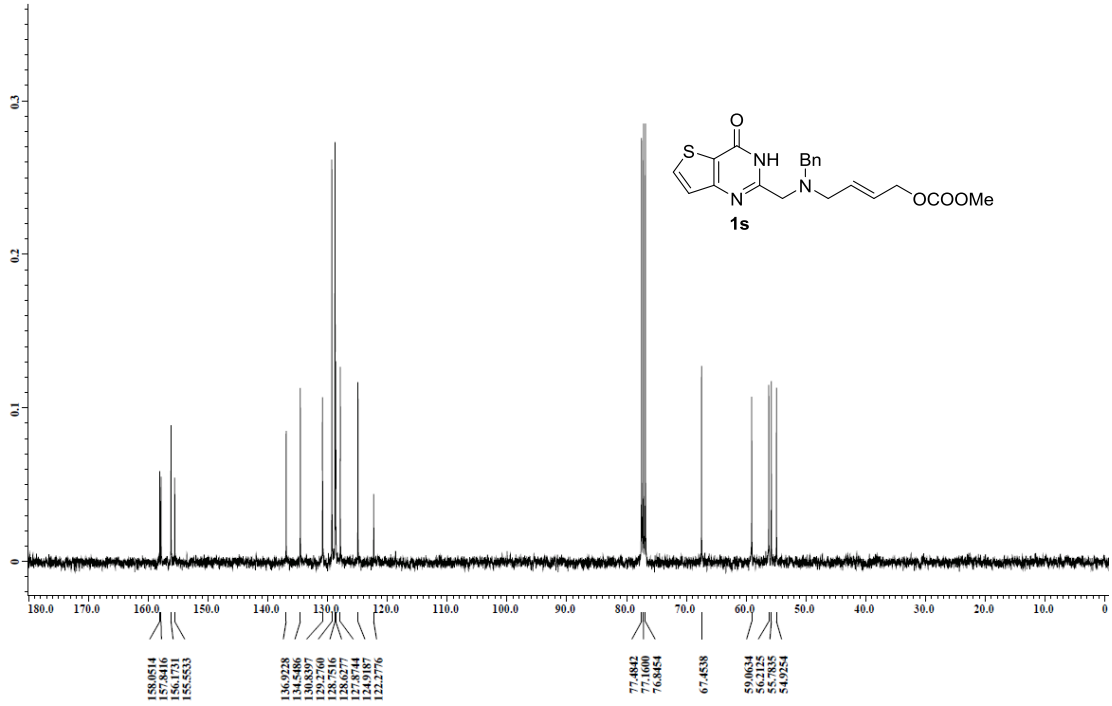
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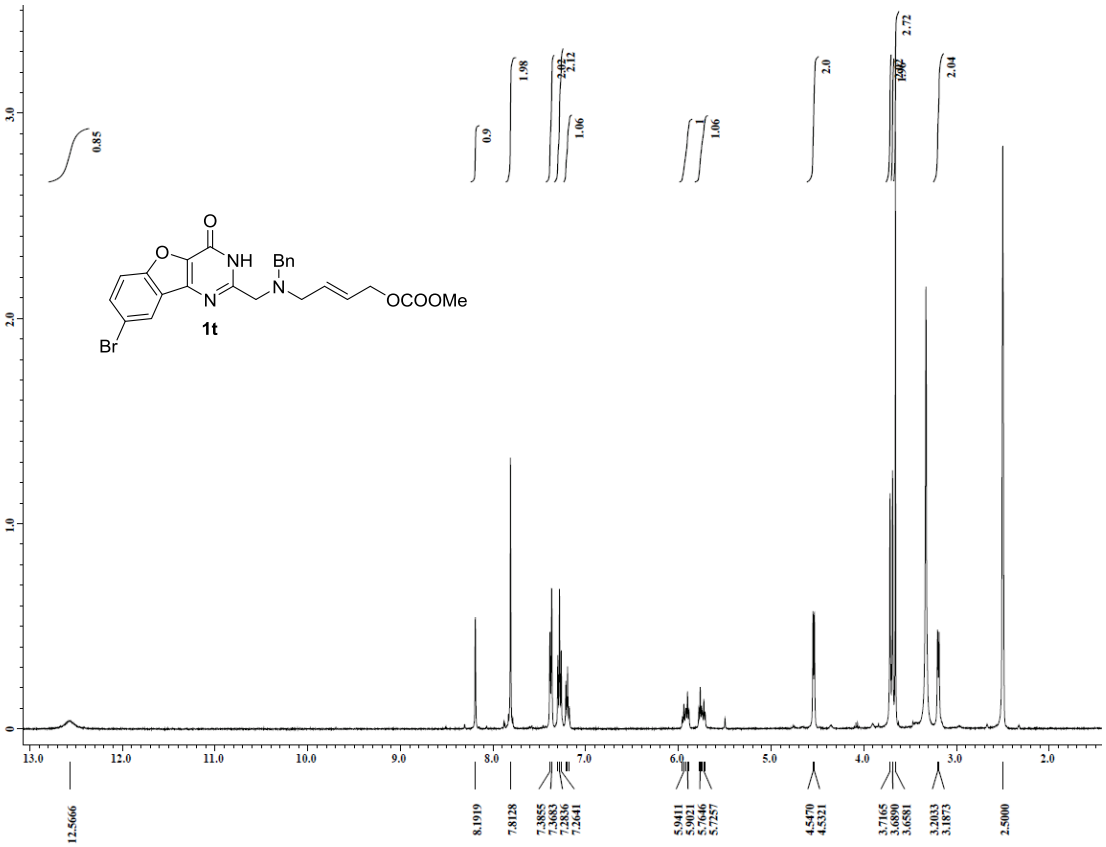
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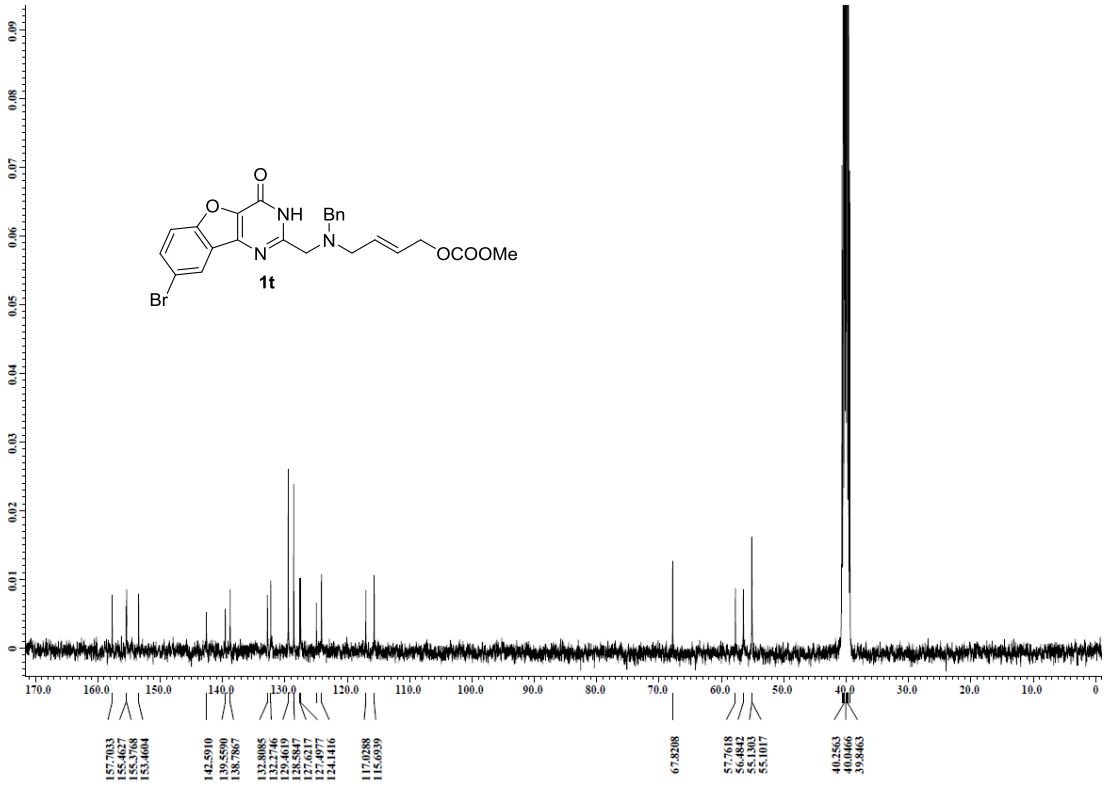
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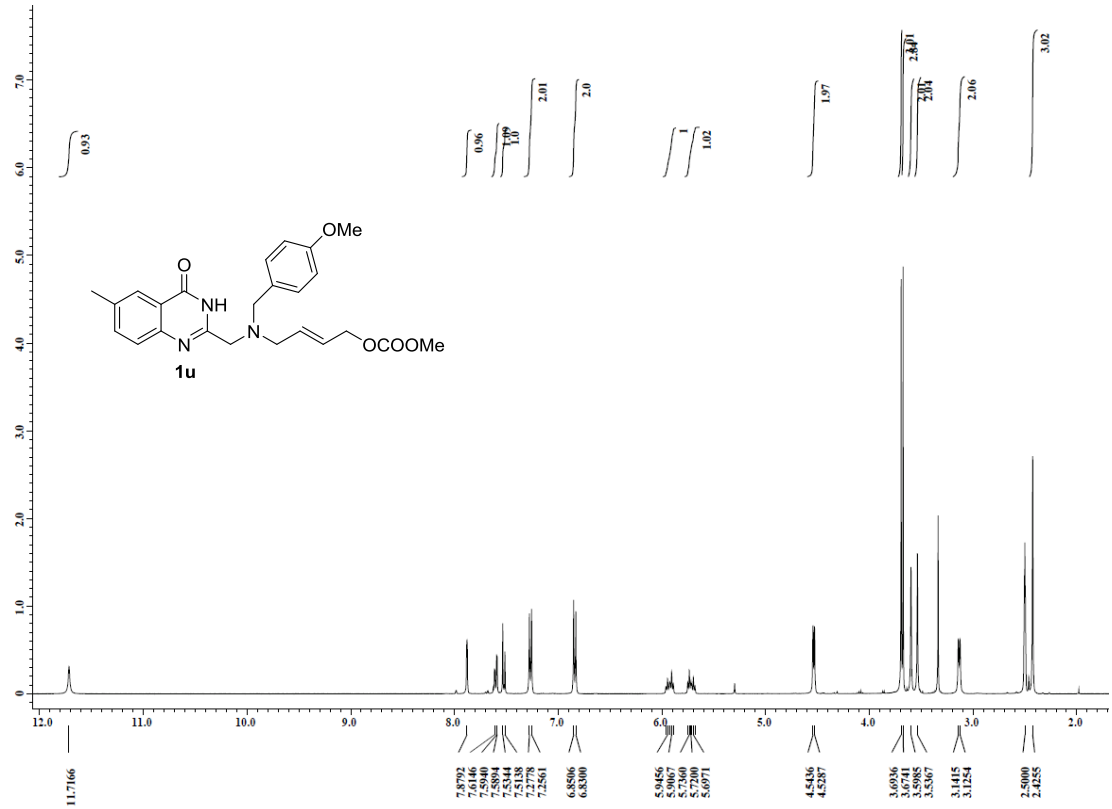
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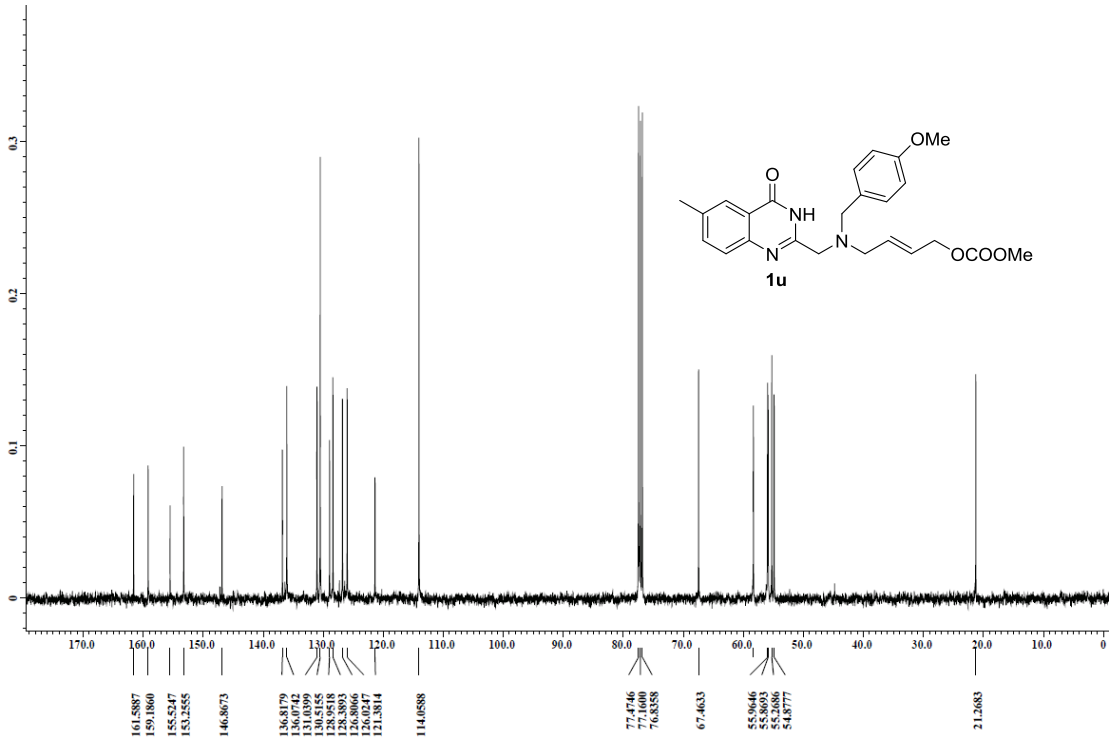
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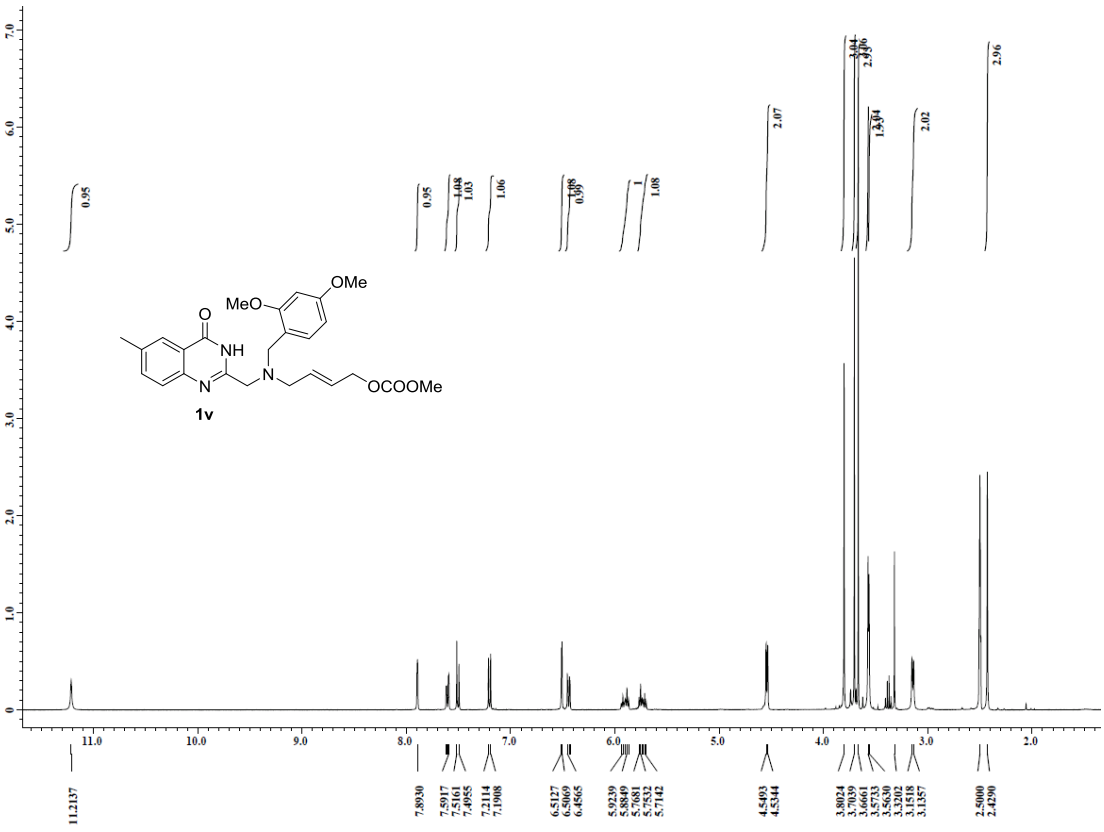
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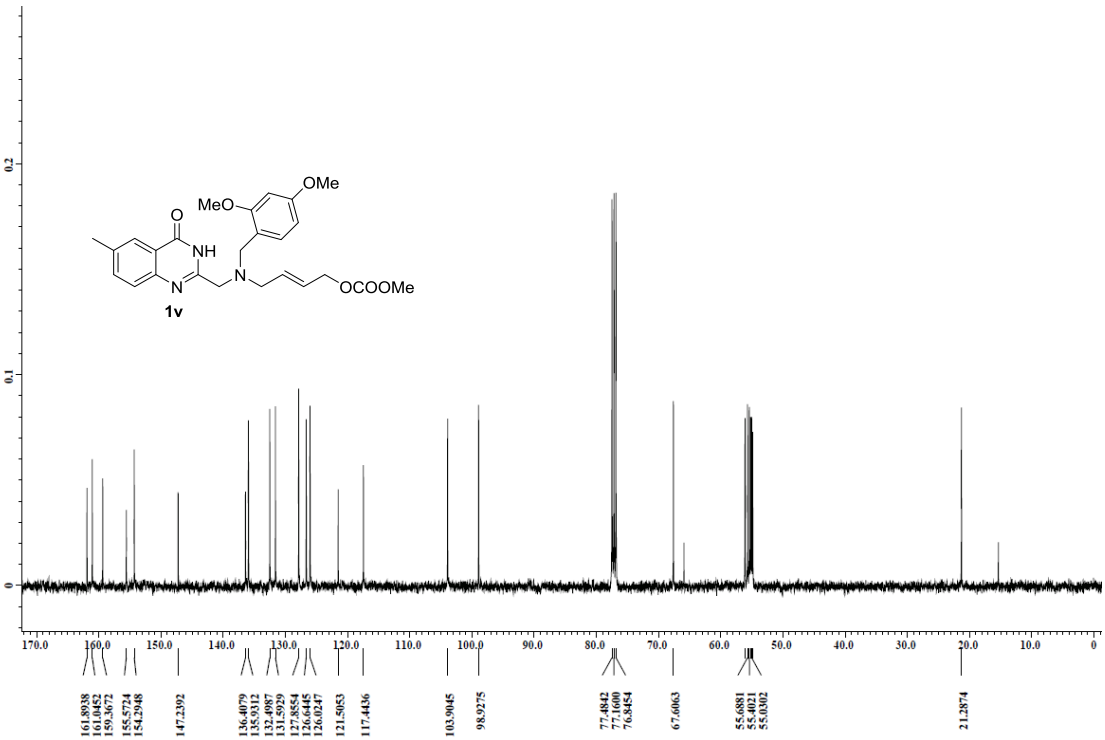
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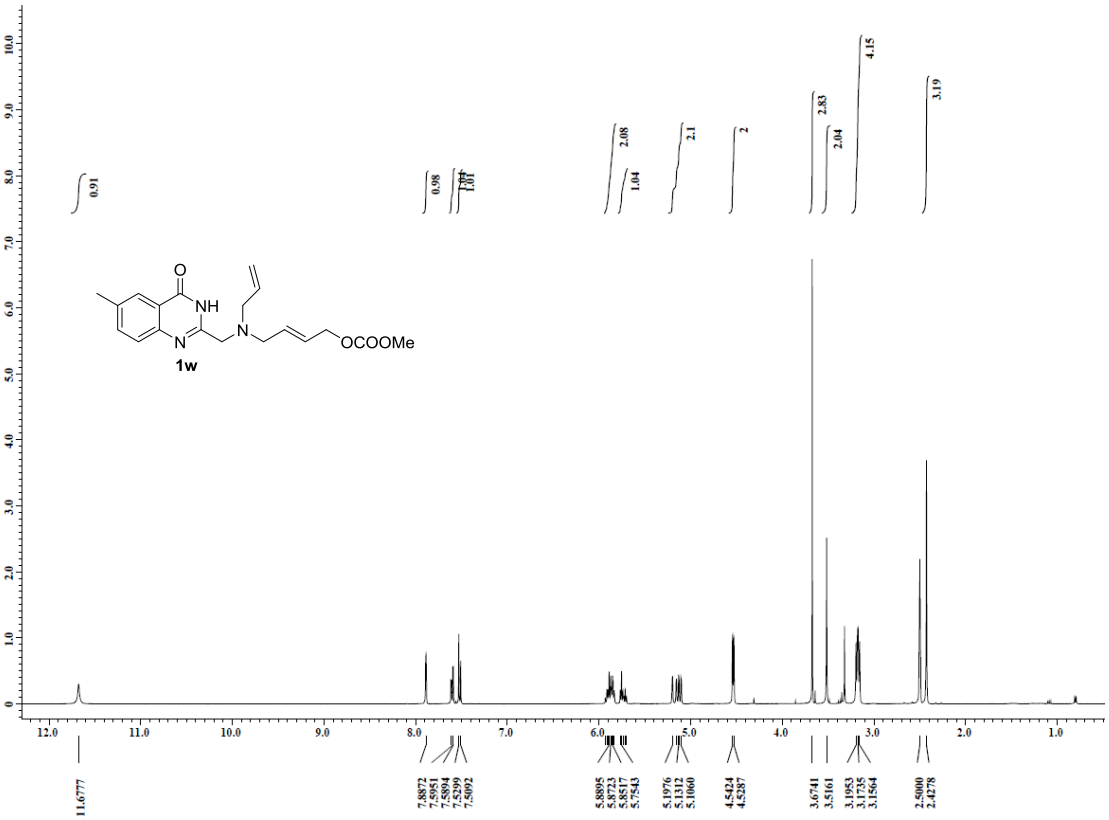
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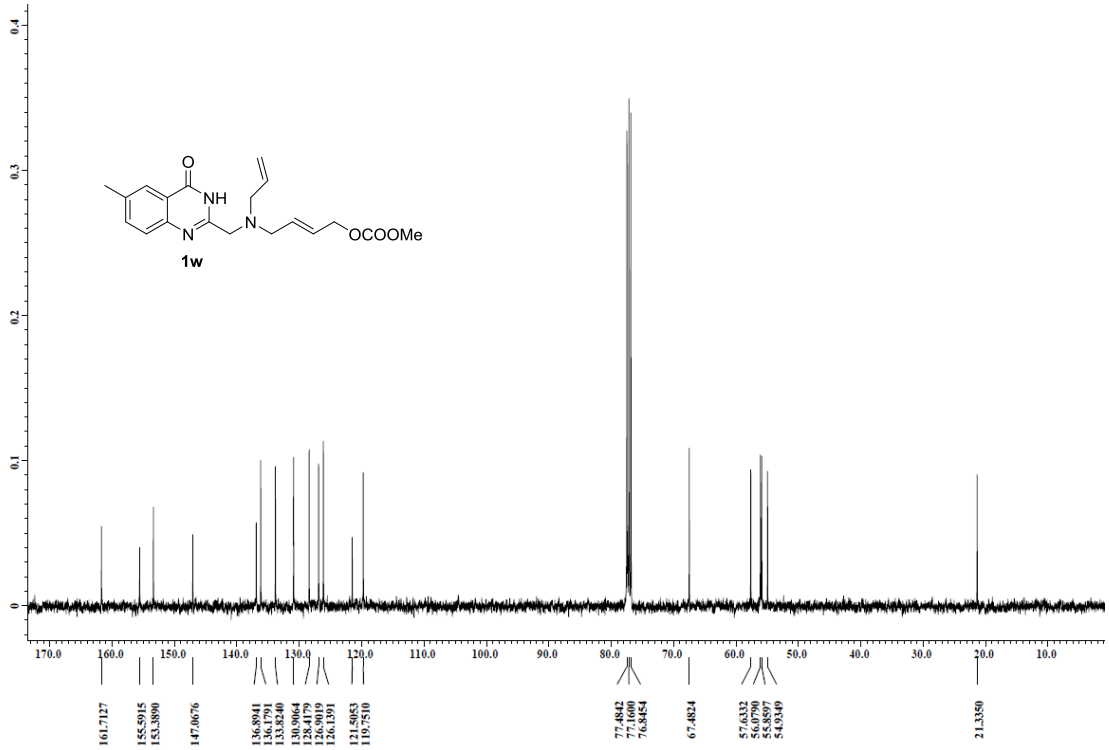
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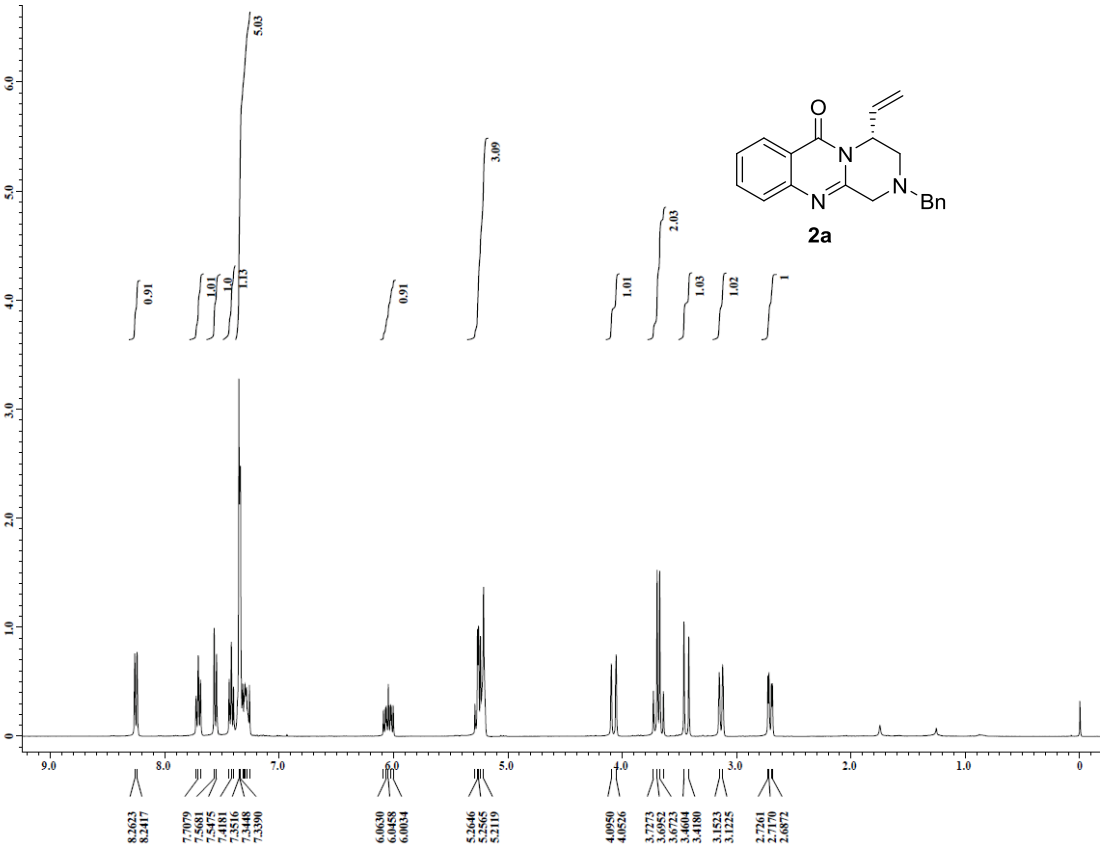
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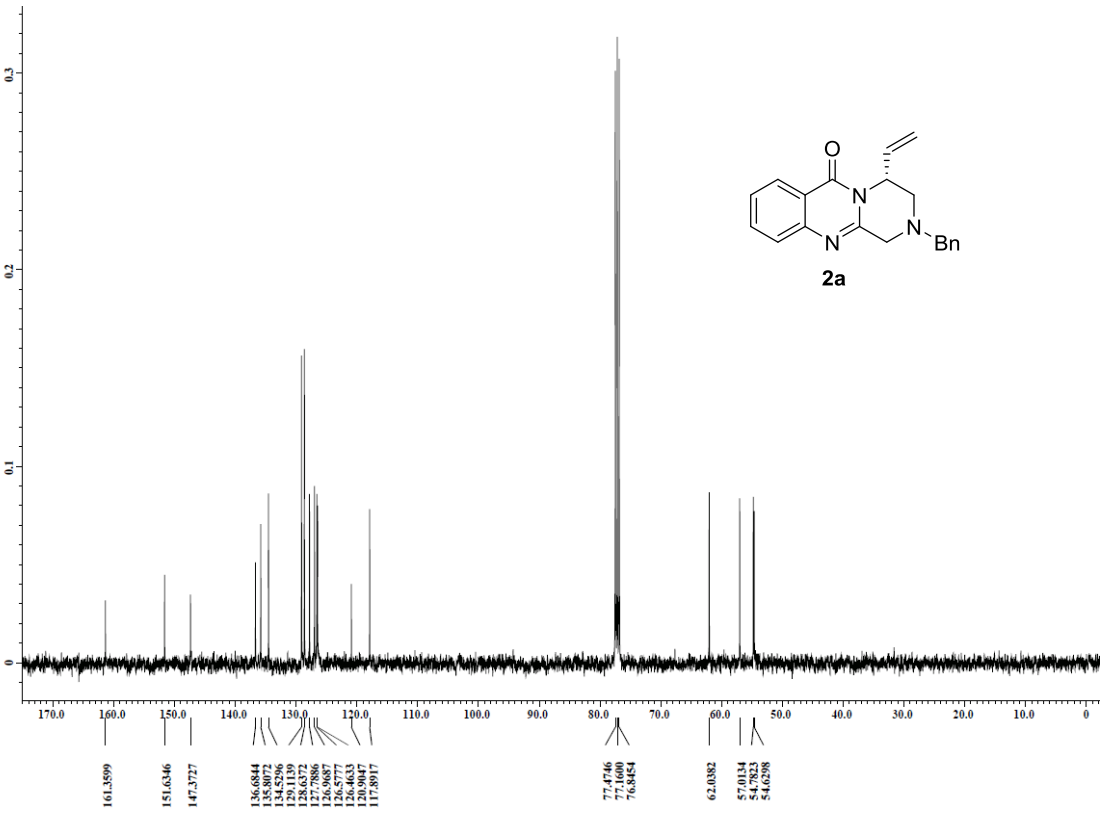
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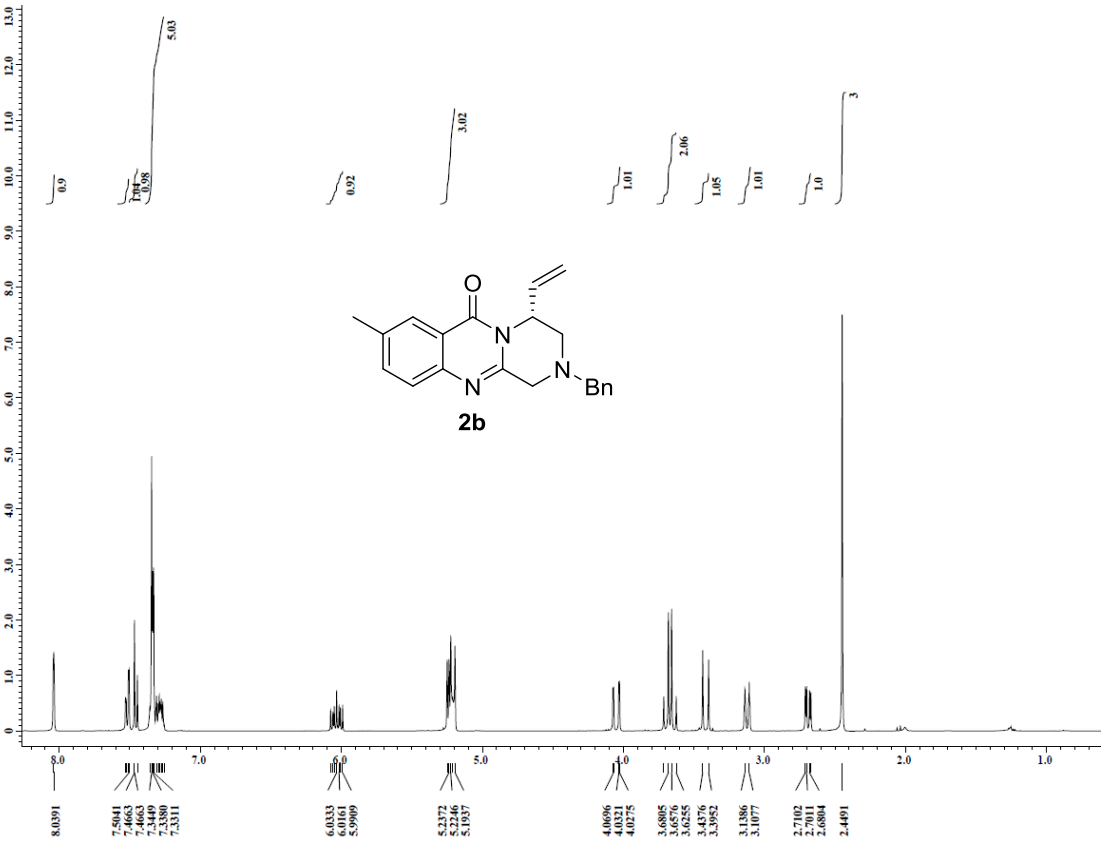
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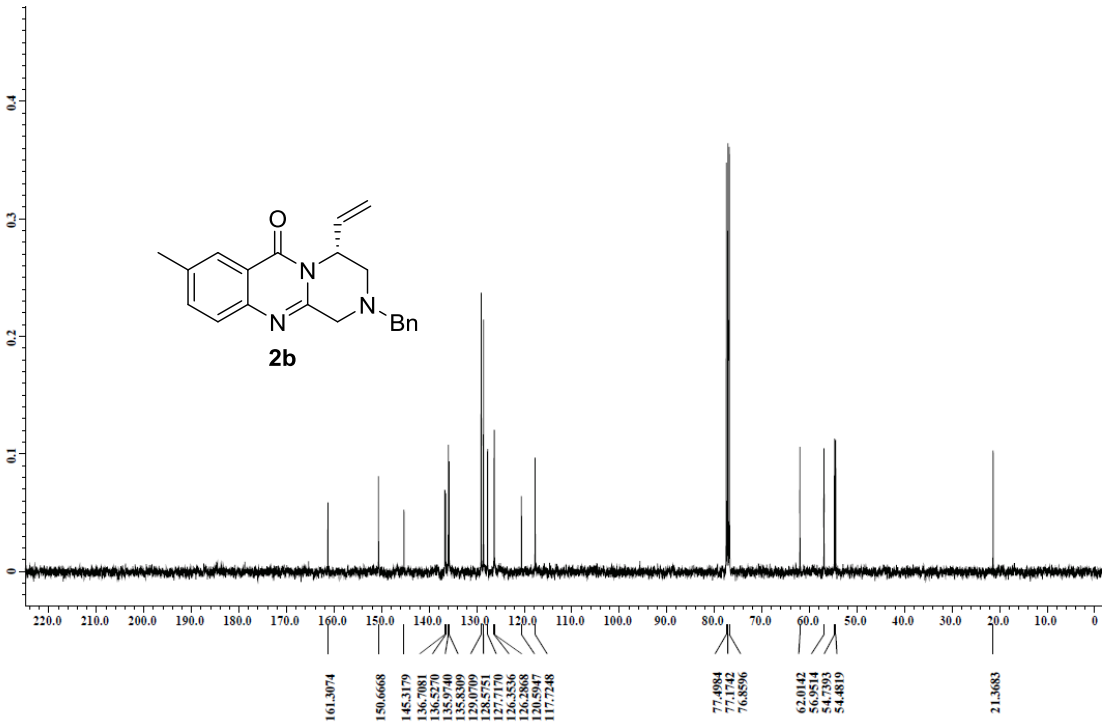
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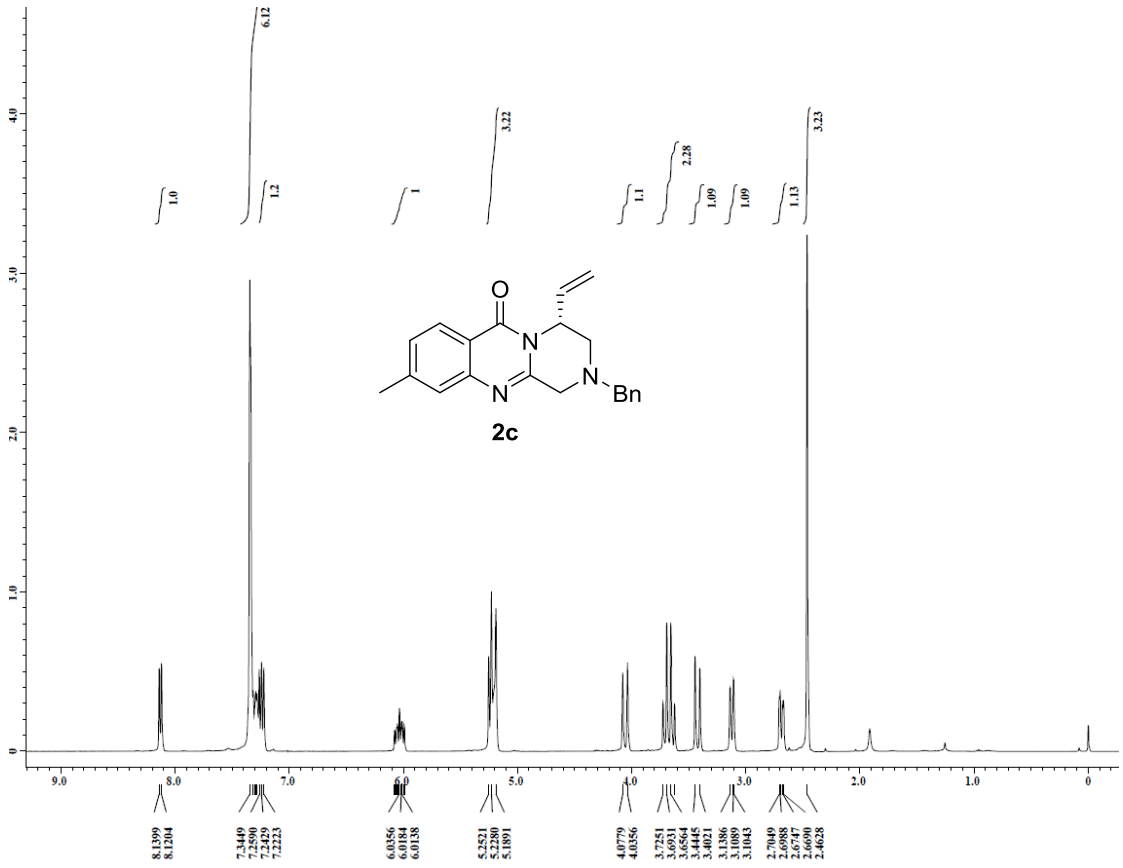
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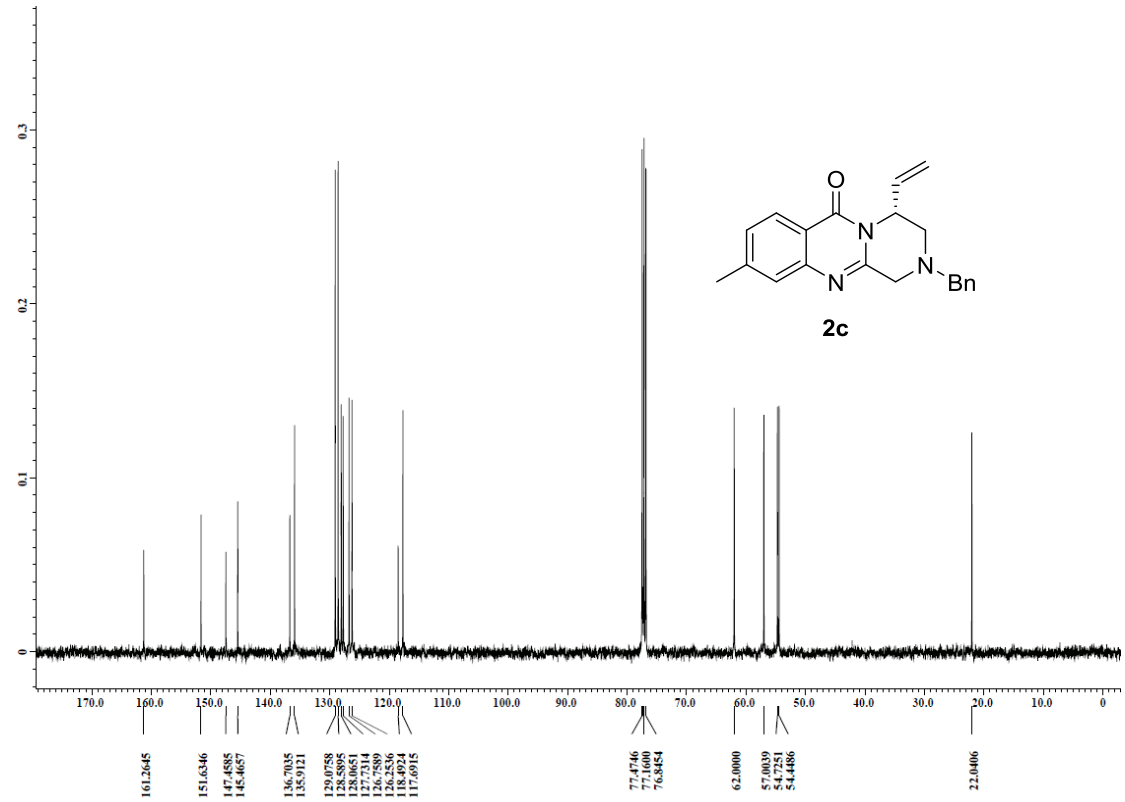
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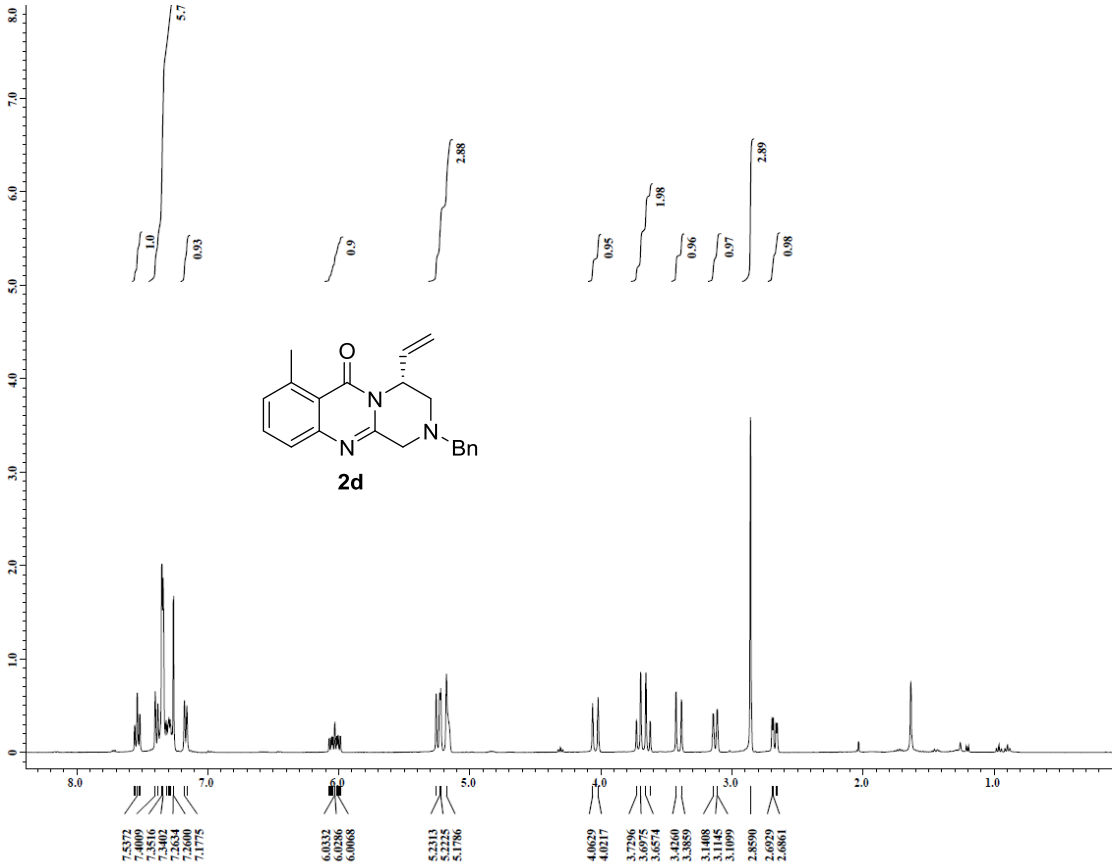
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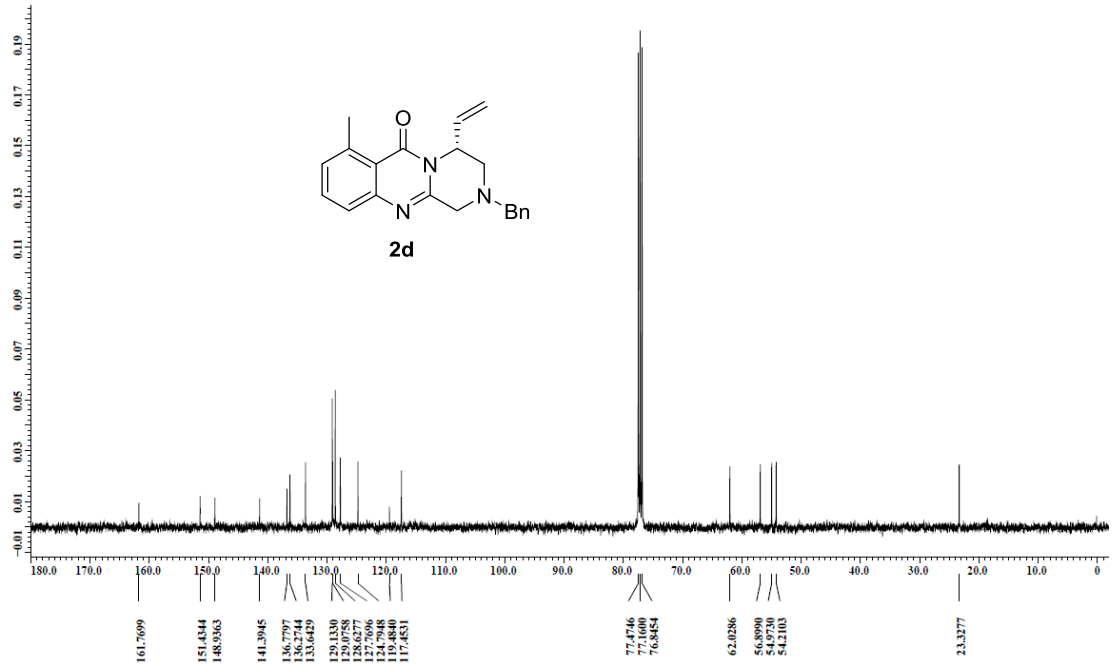
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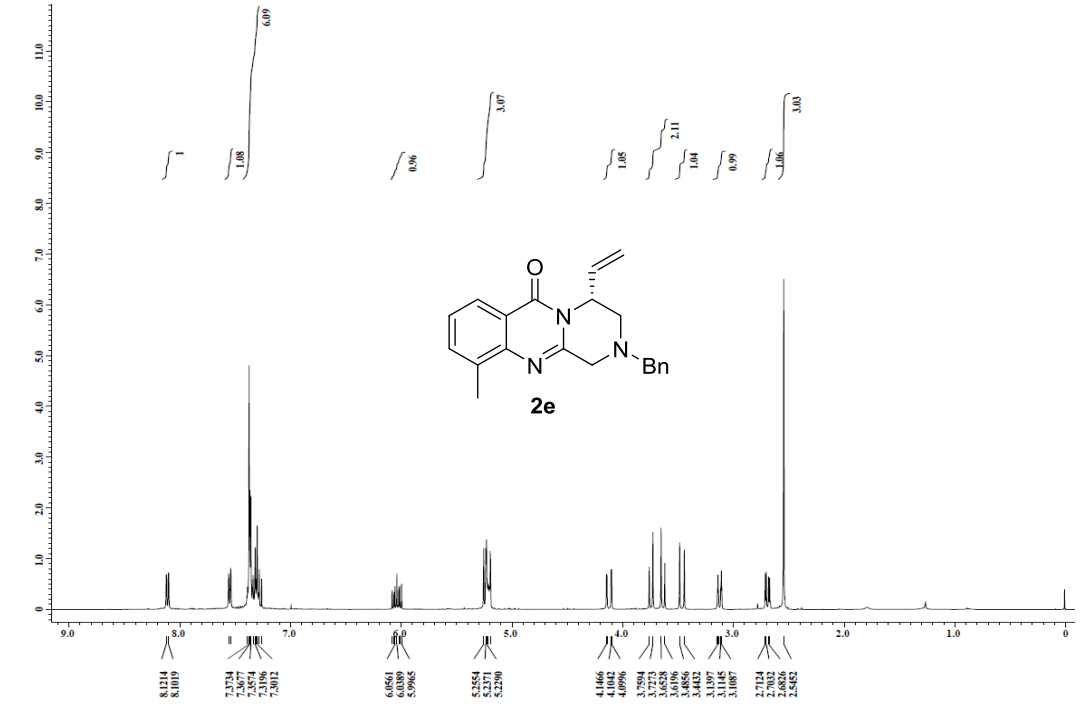
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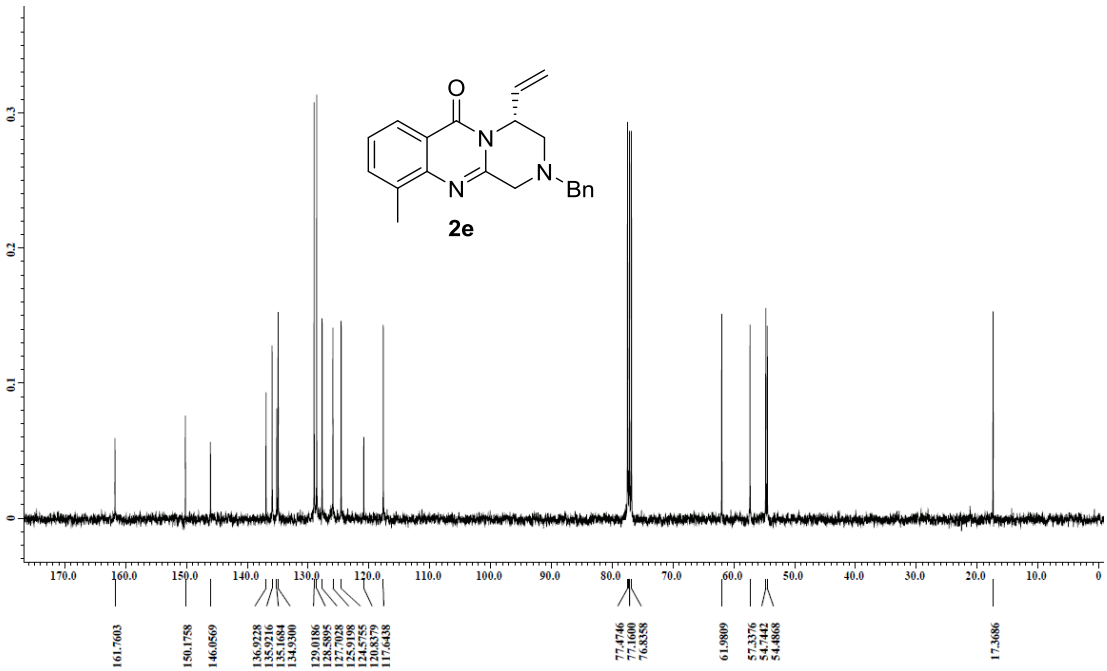
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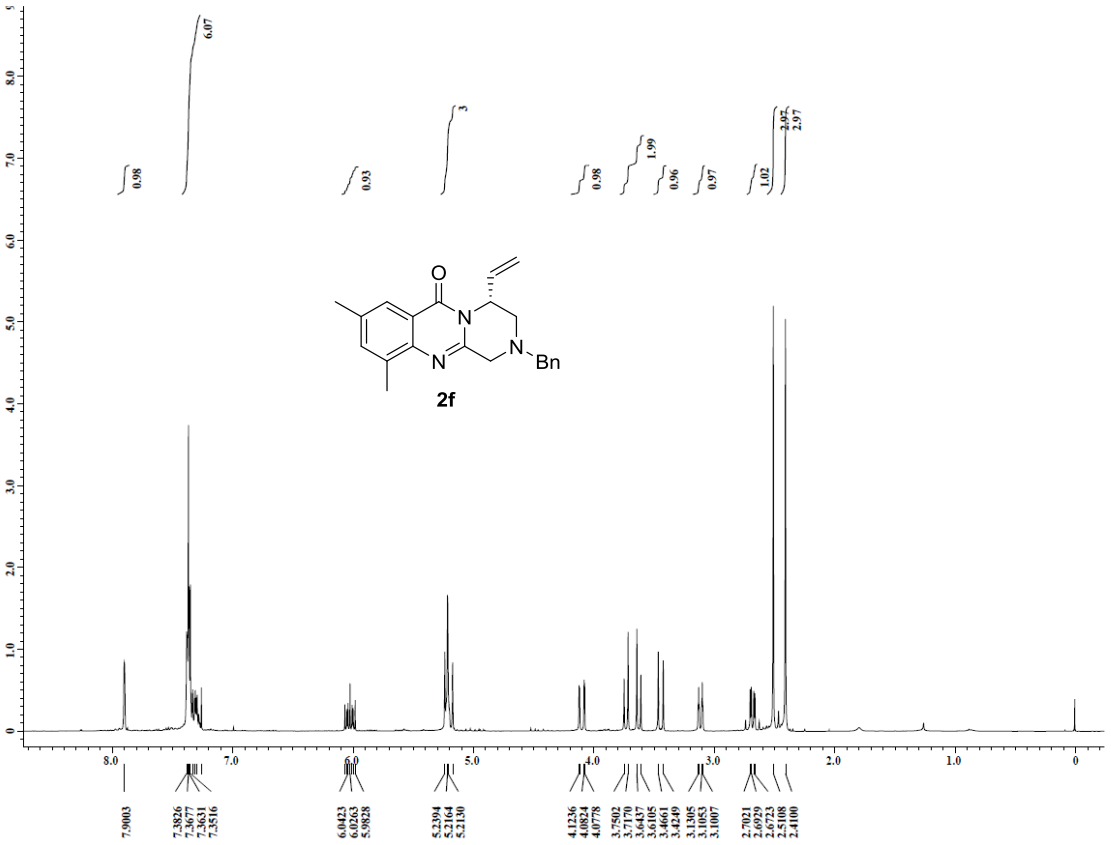
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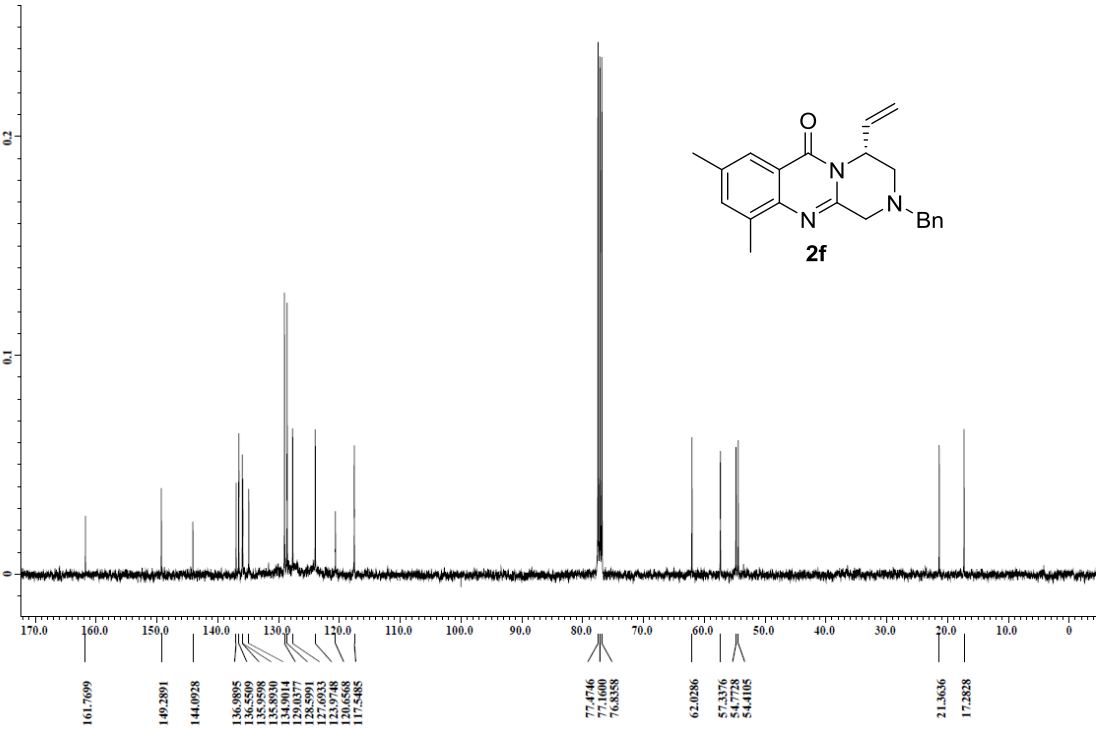
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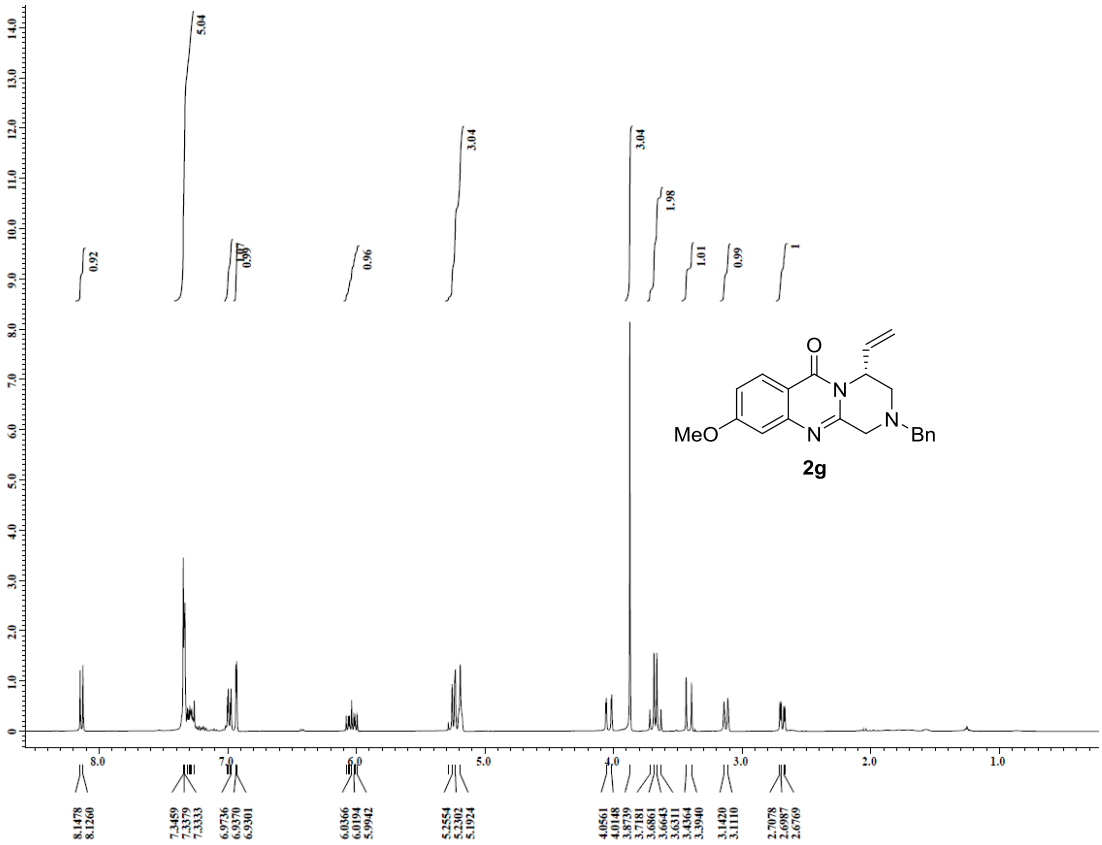
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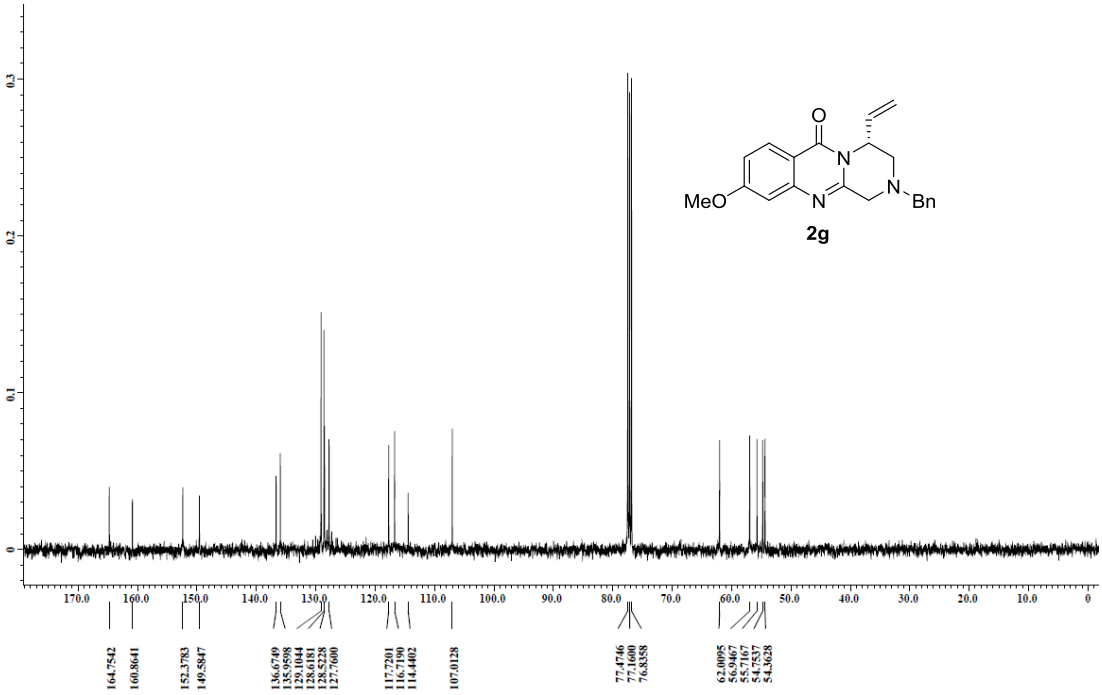
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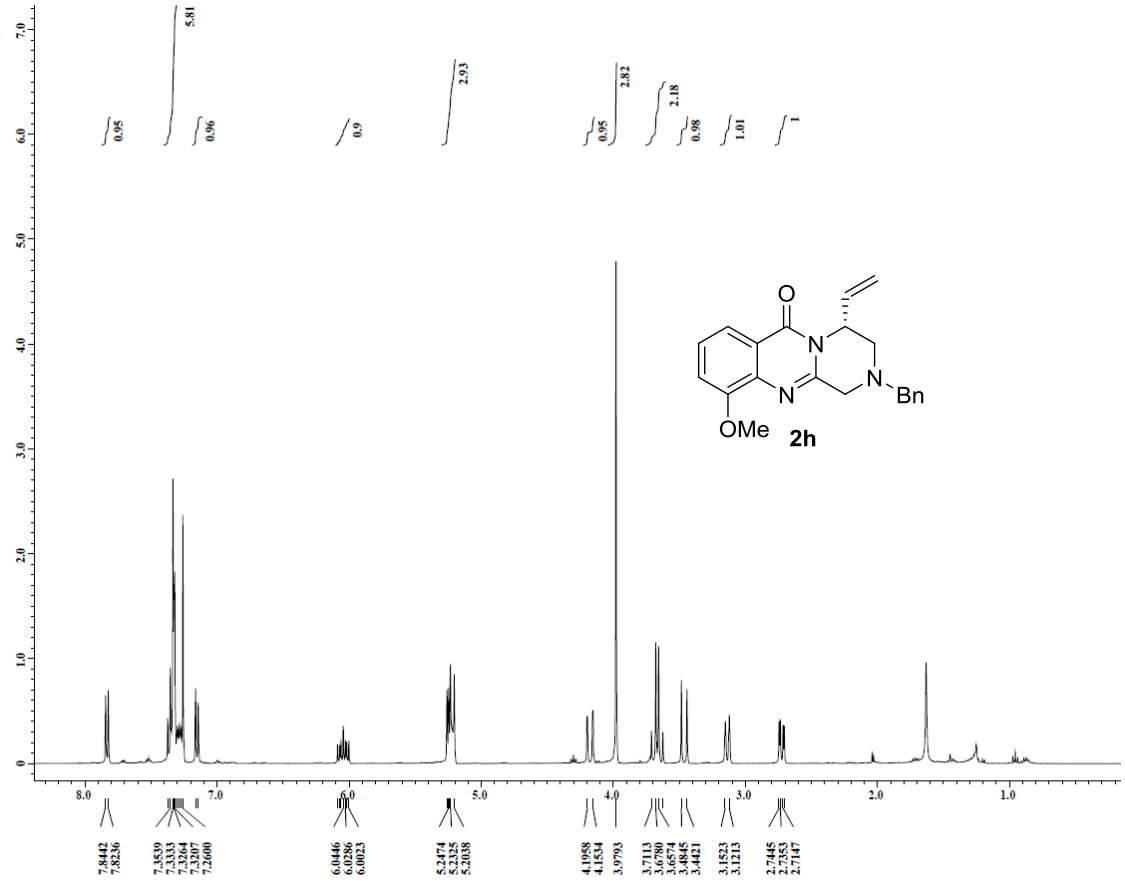
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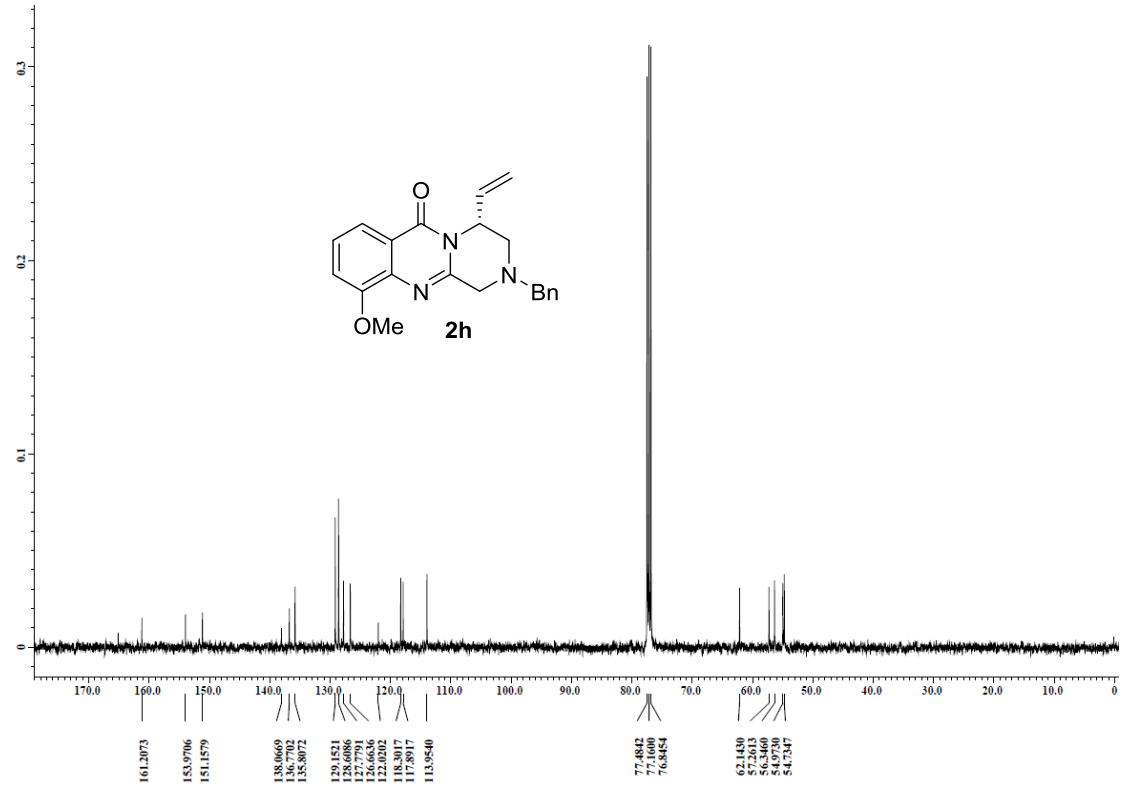
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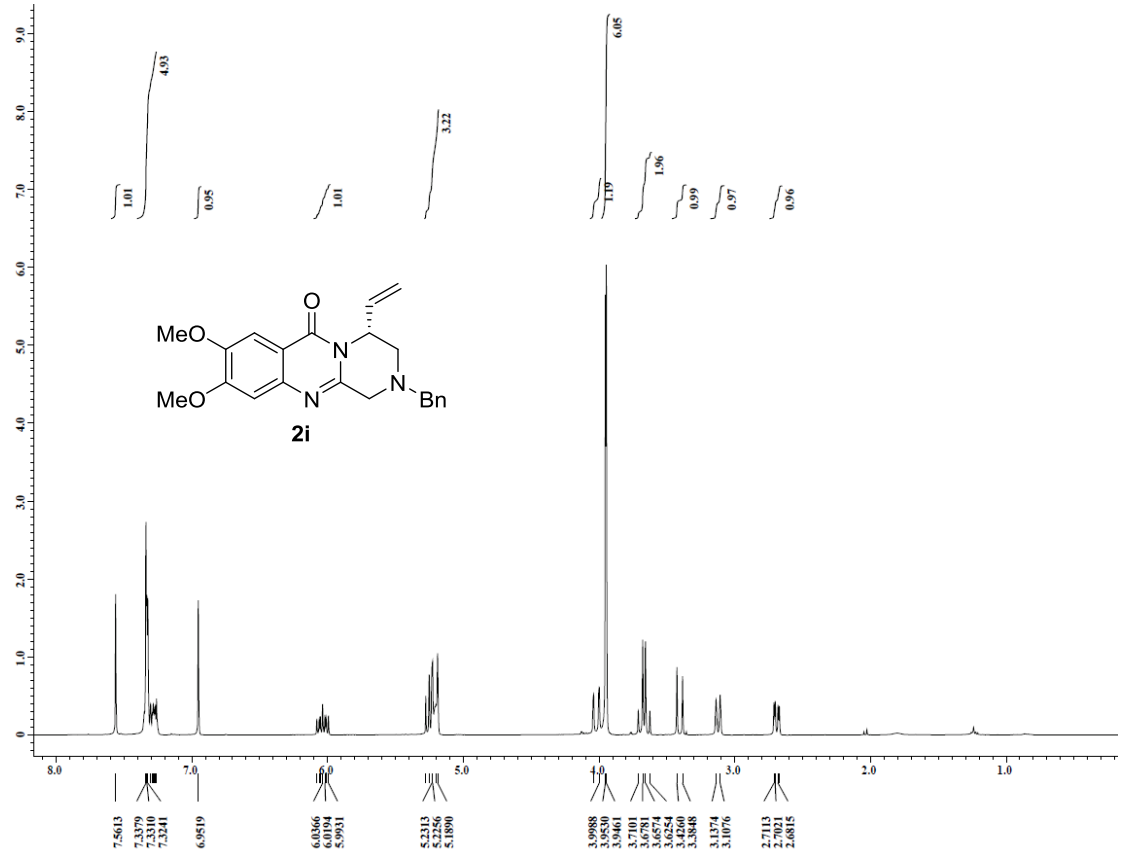
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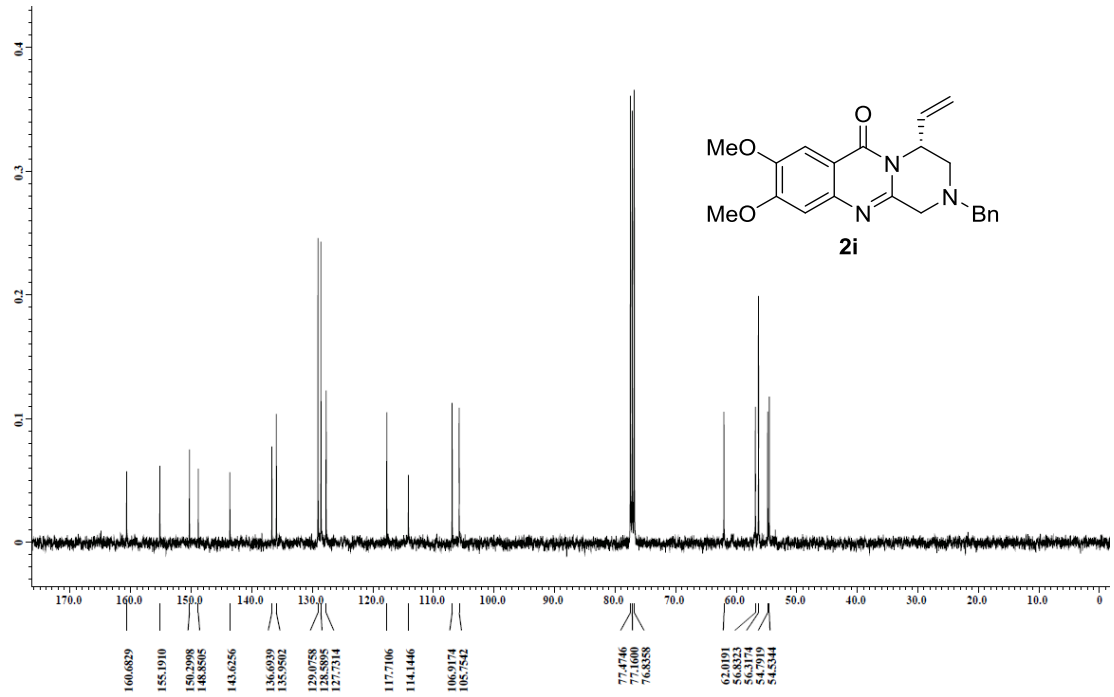
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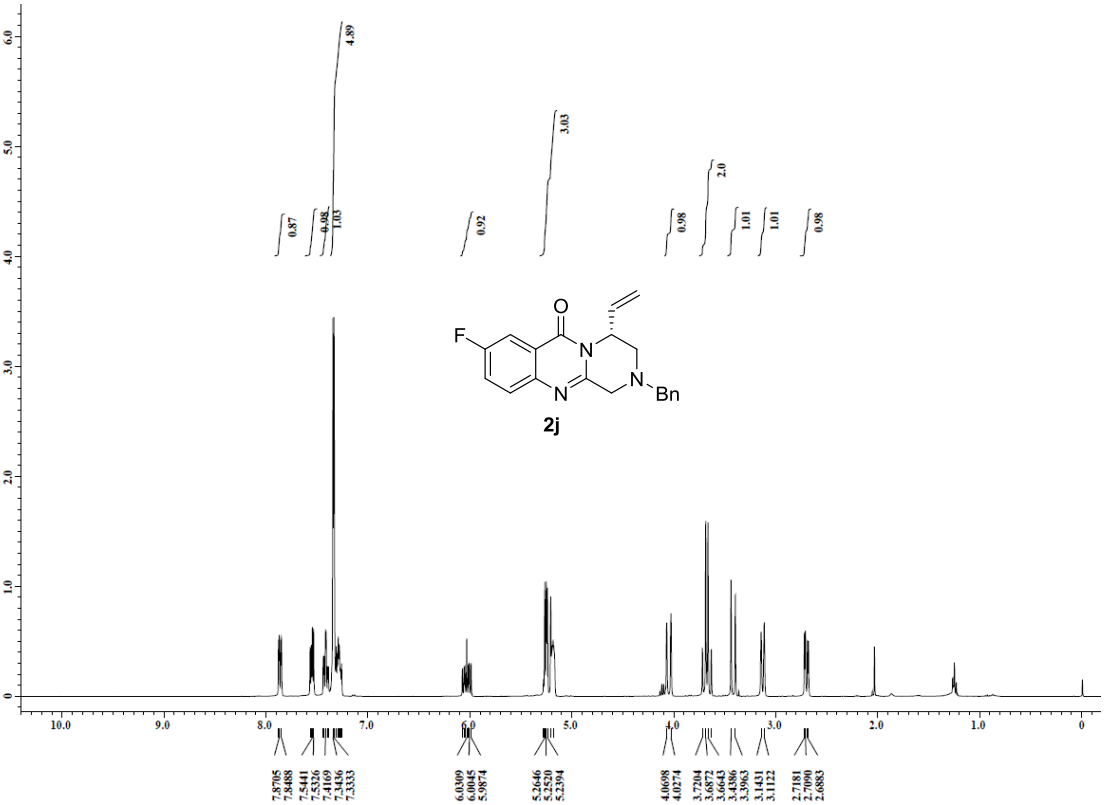
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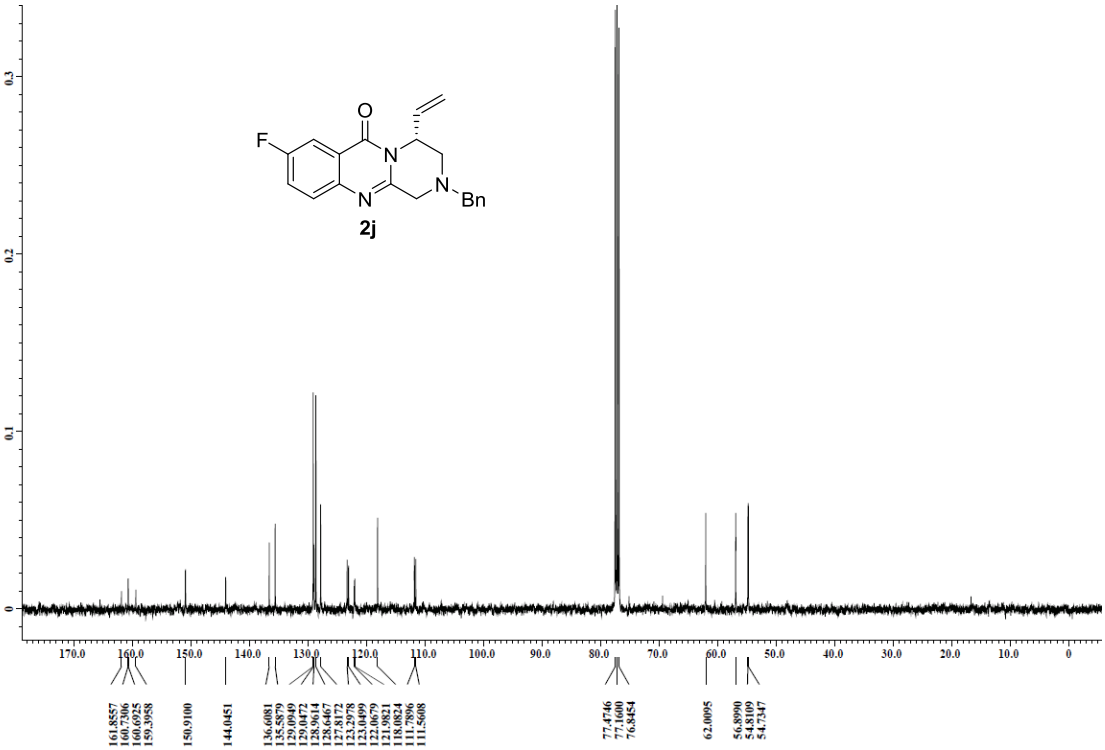
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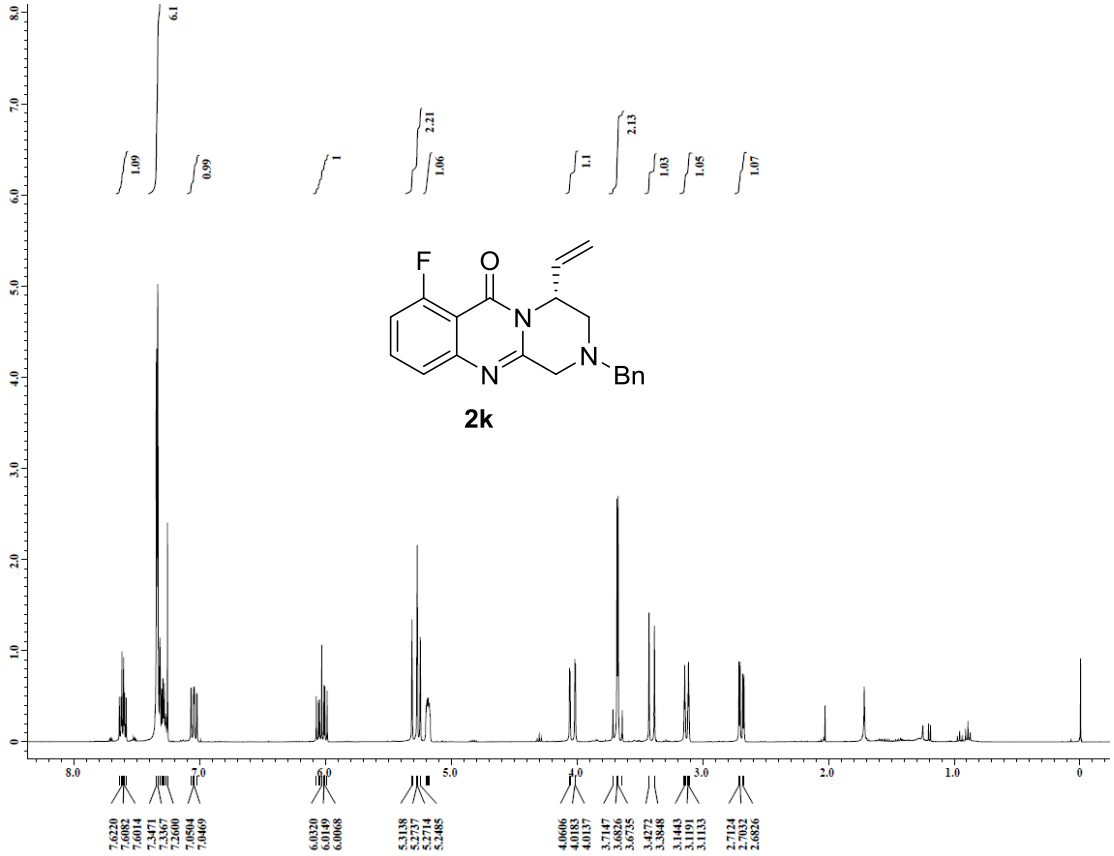

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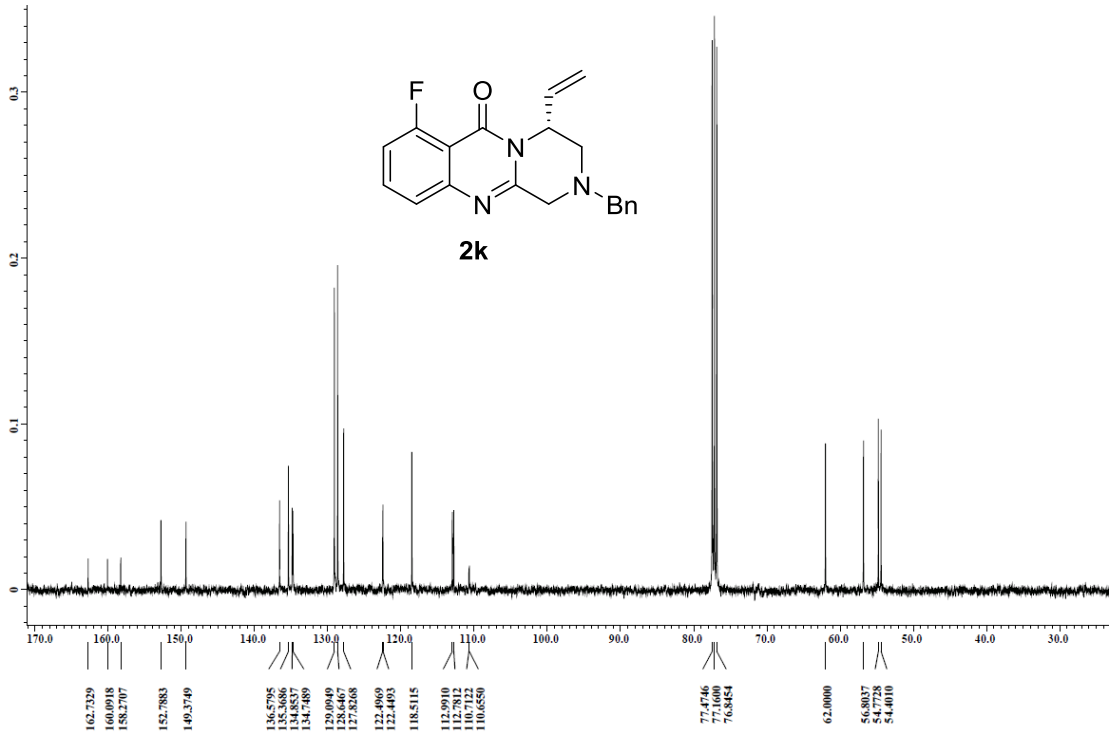

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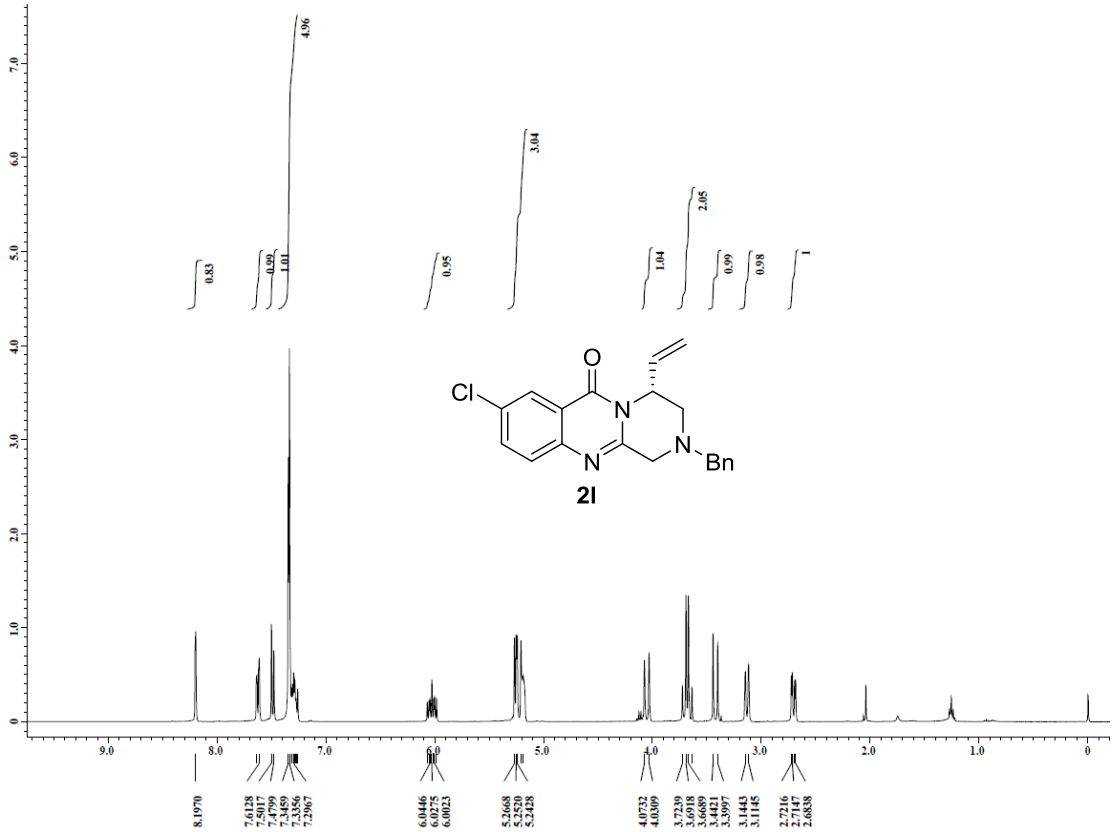
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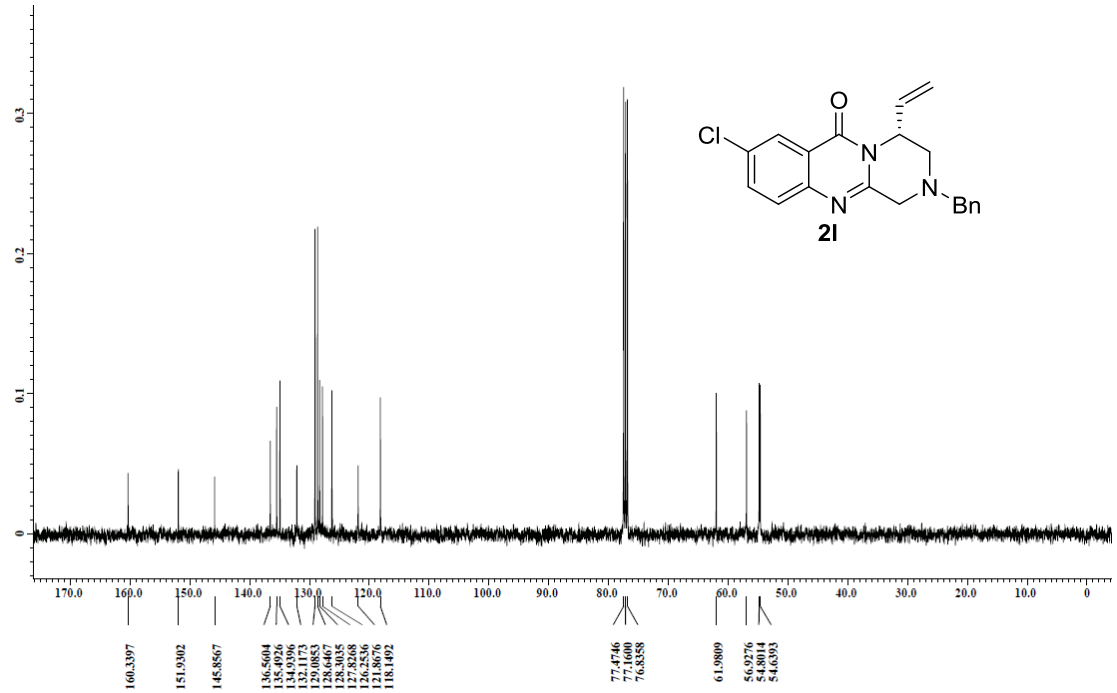
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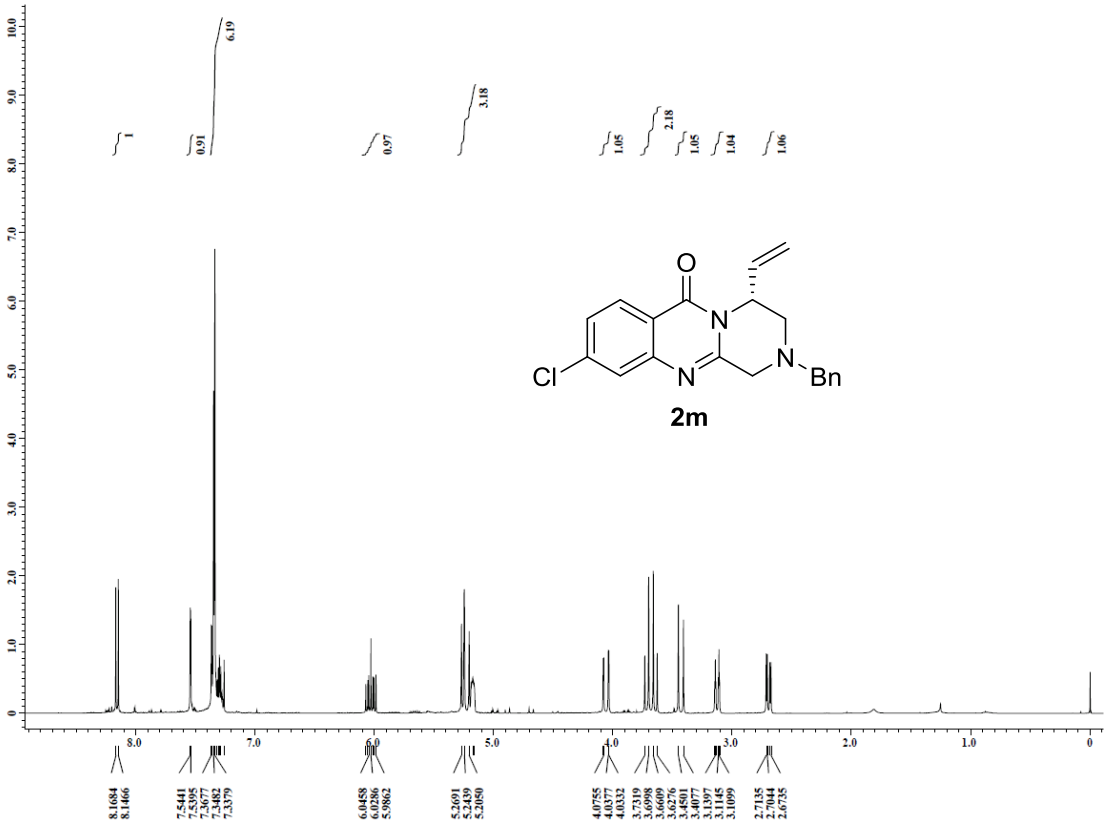
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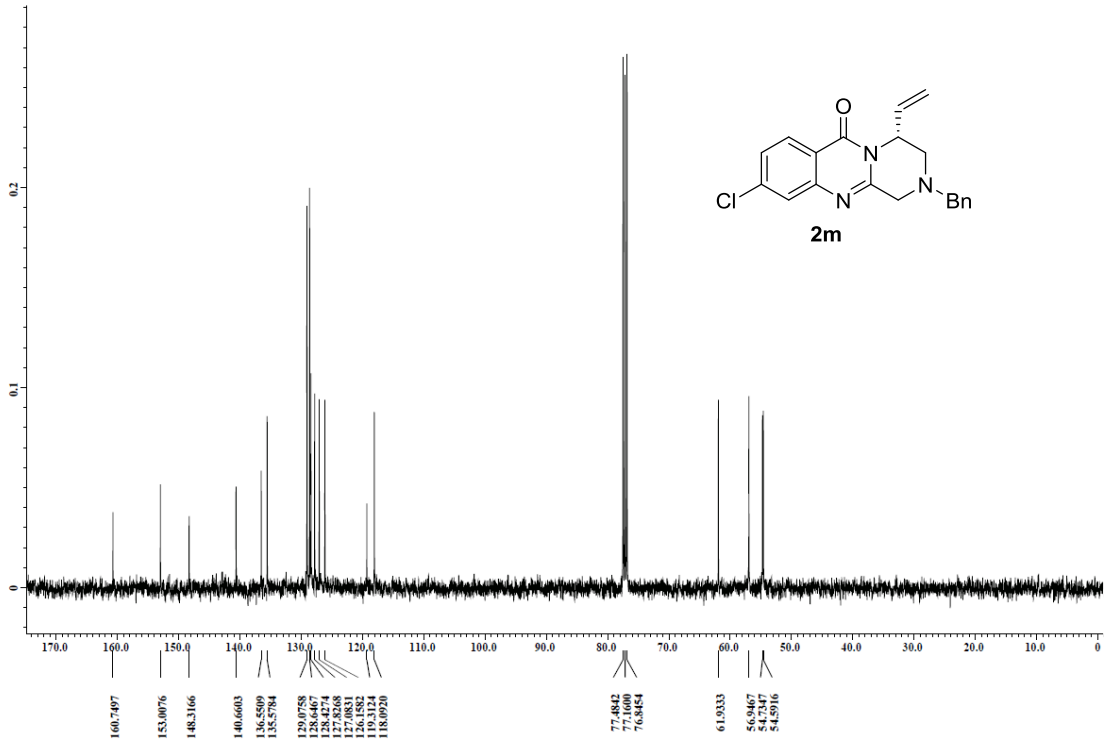
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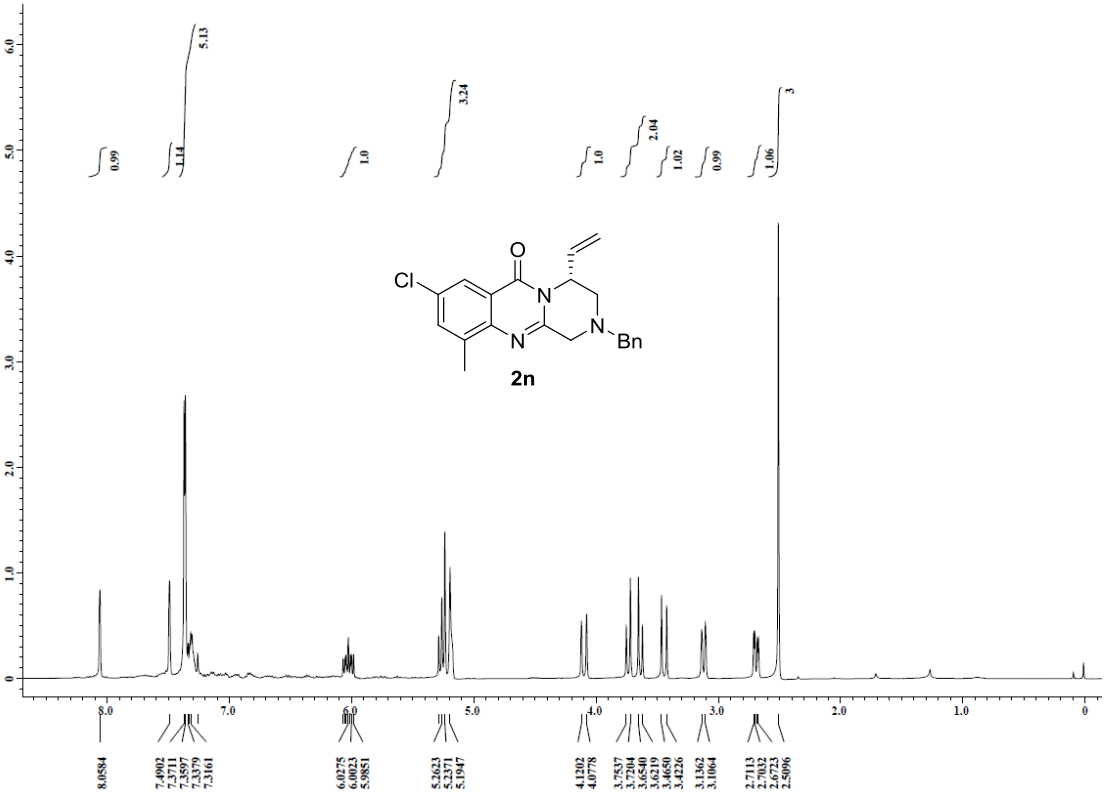
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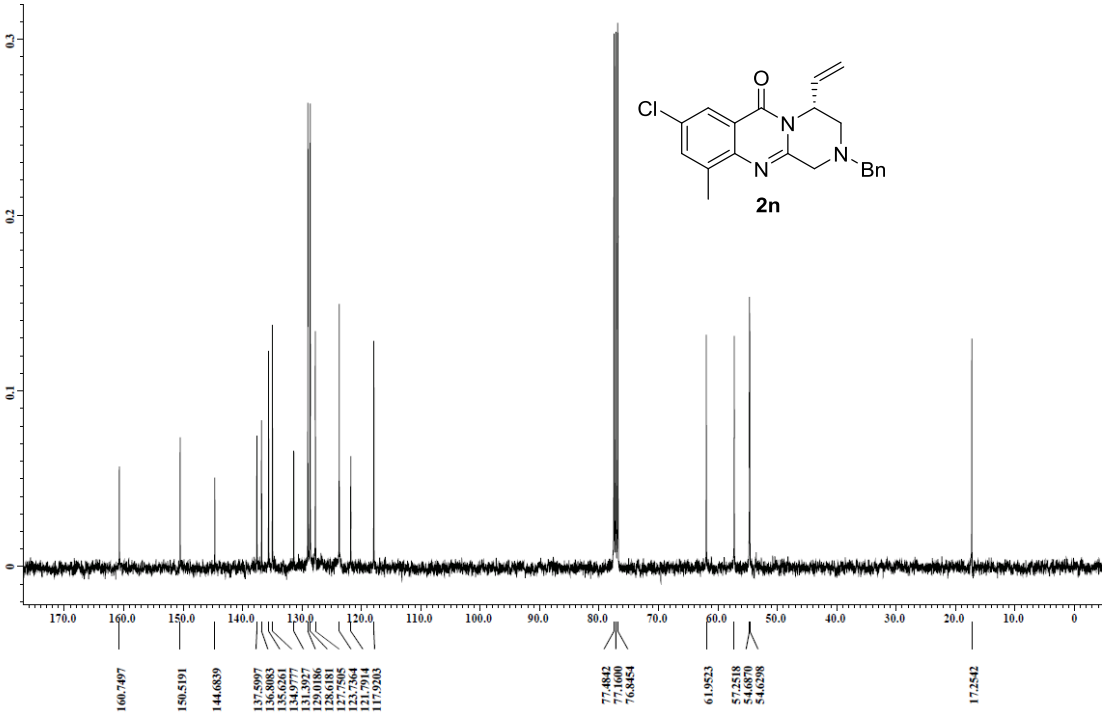
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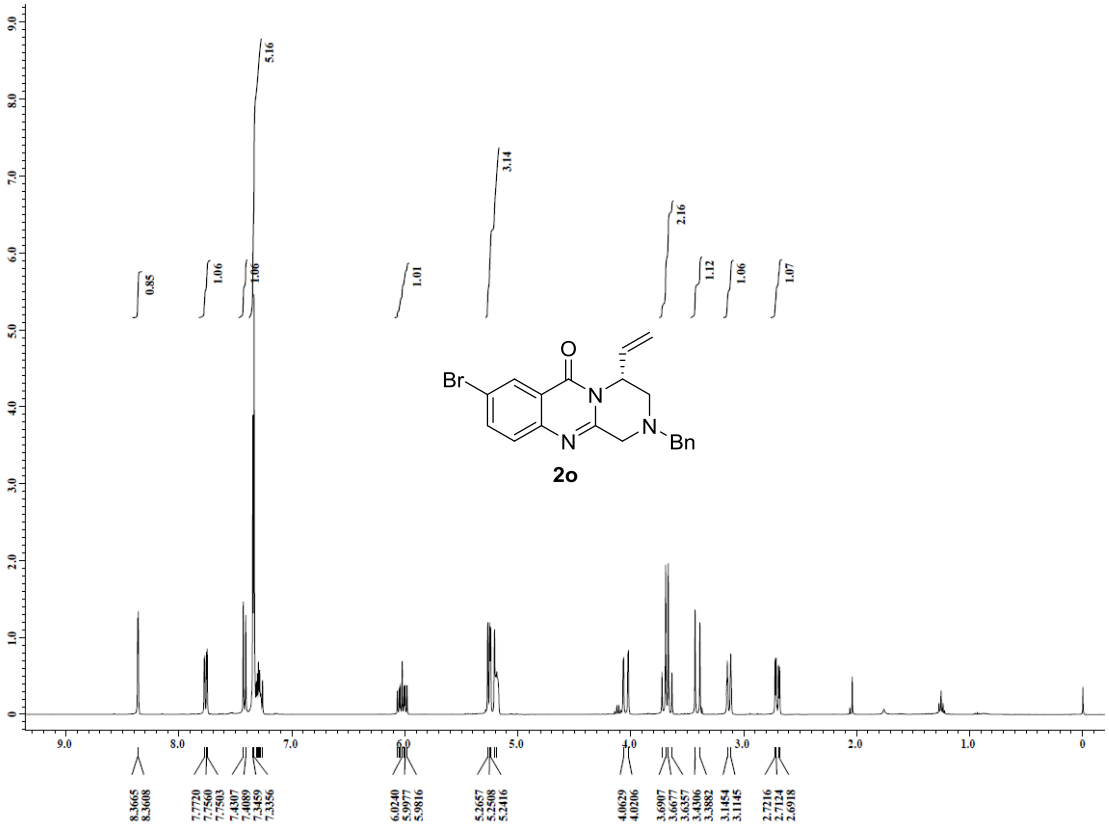
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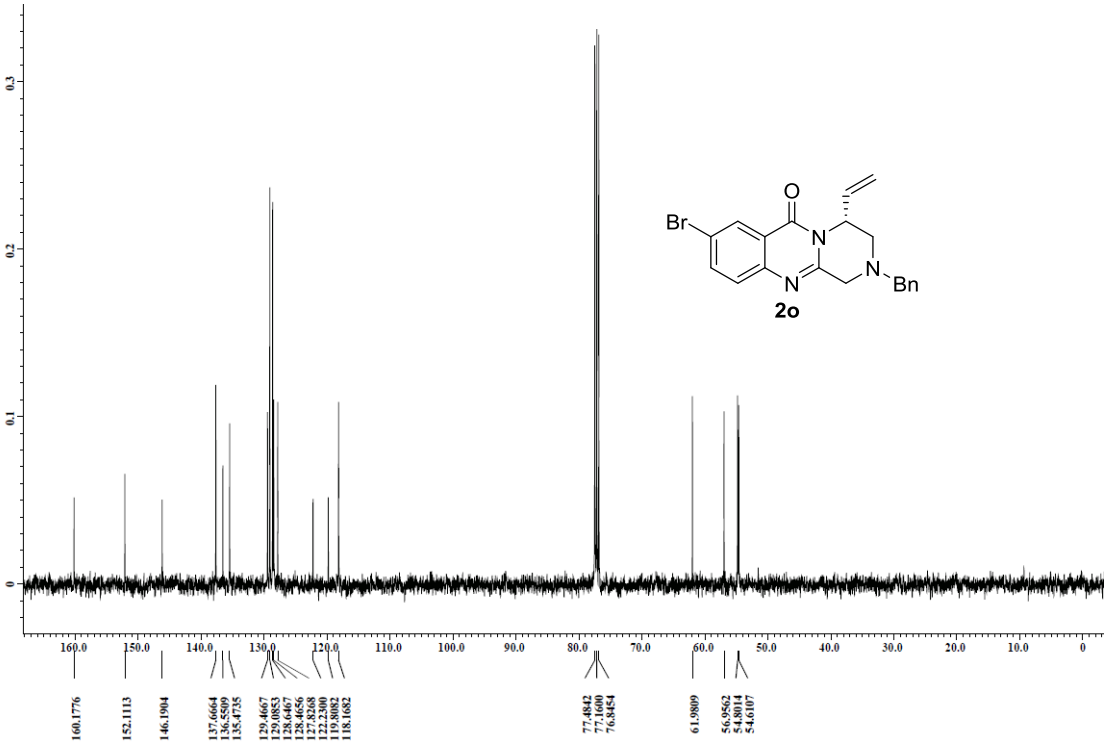
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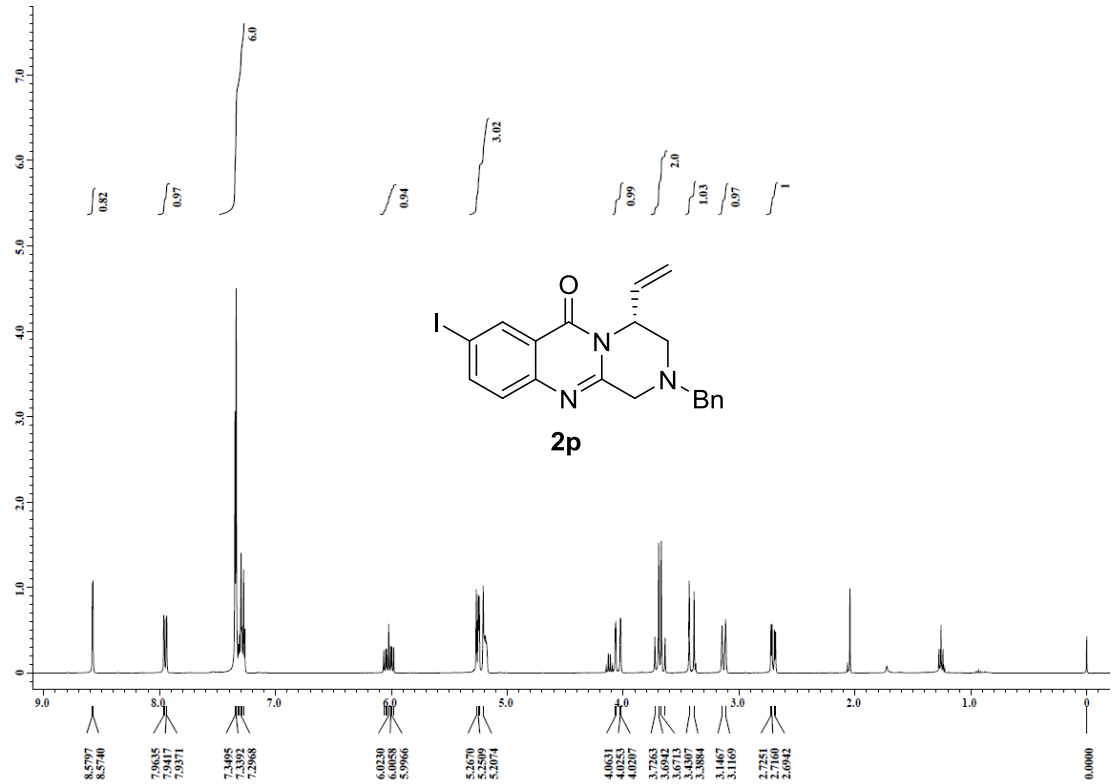

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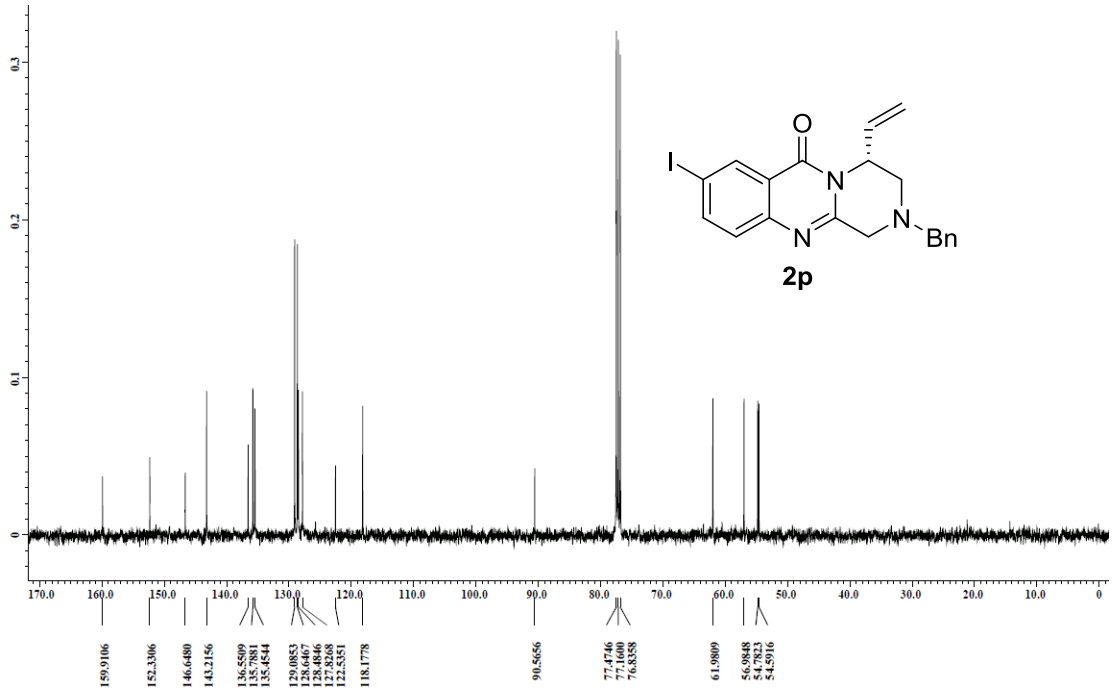

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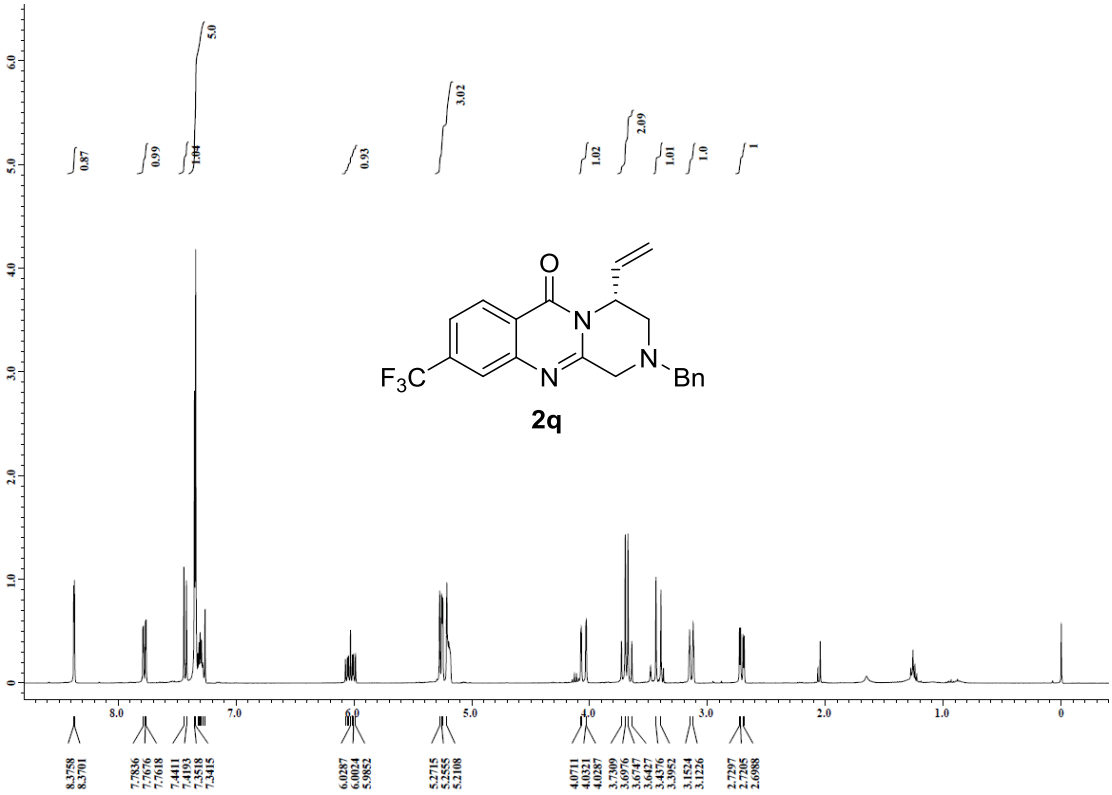
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Bn
F3C
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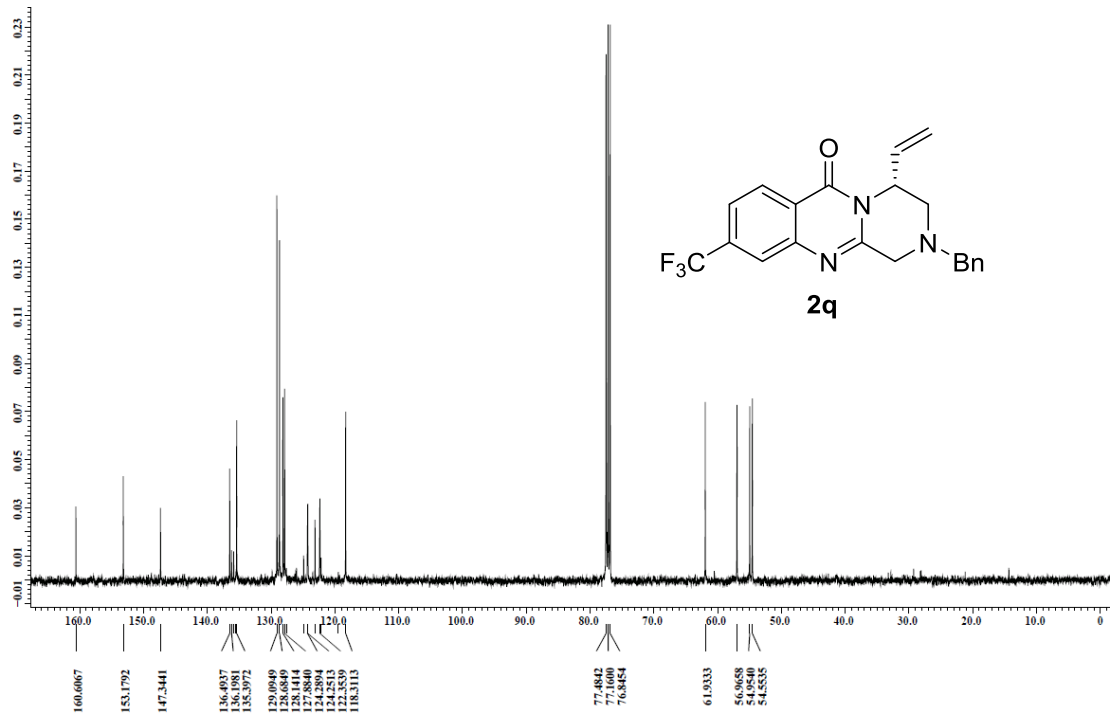
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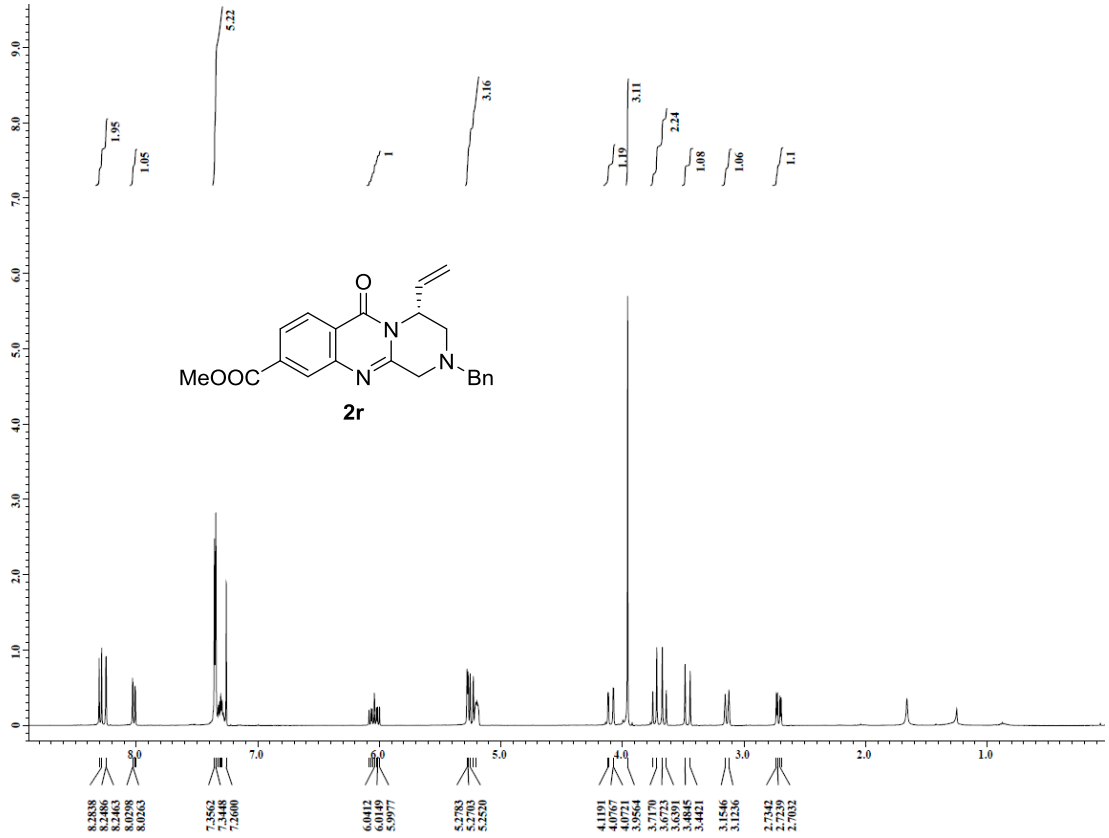
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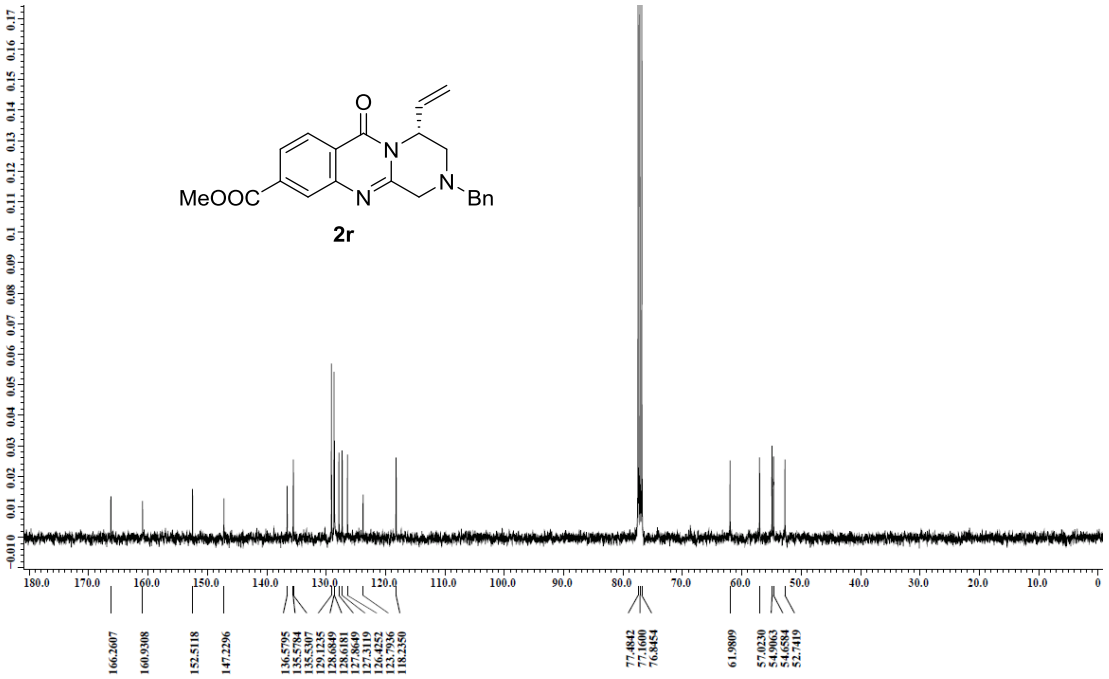
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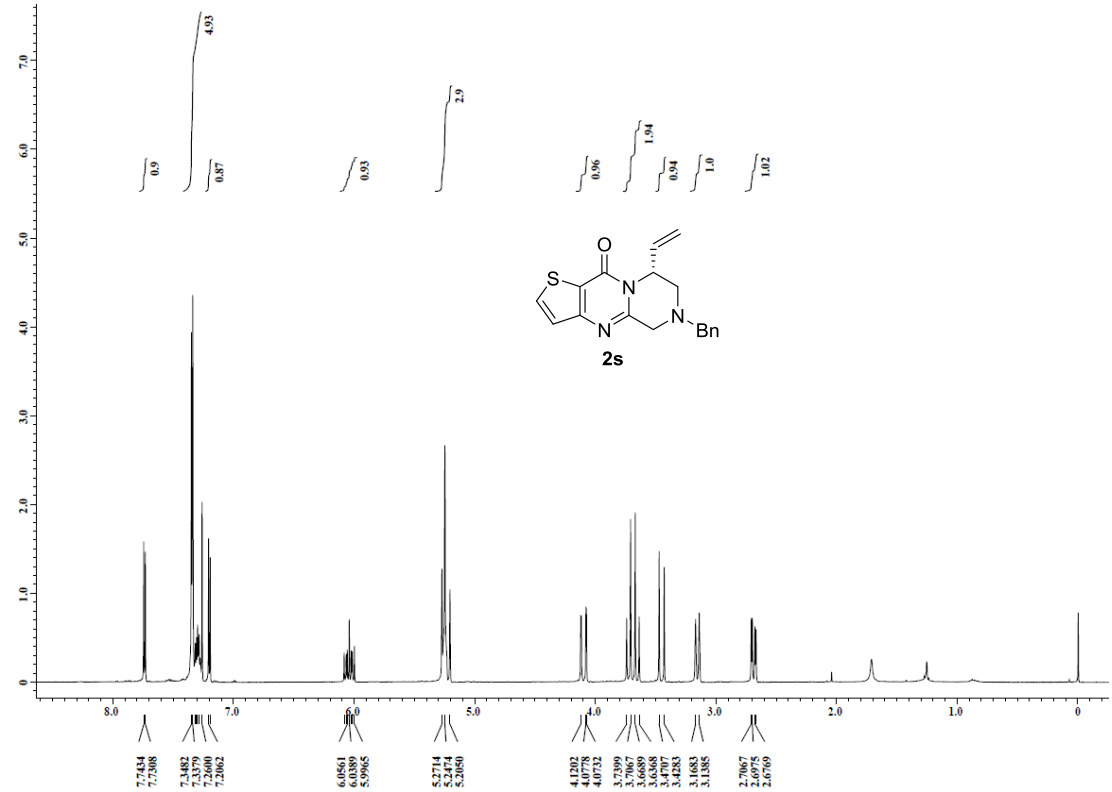
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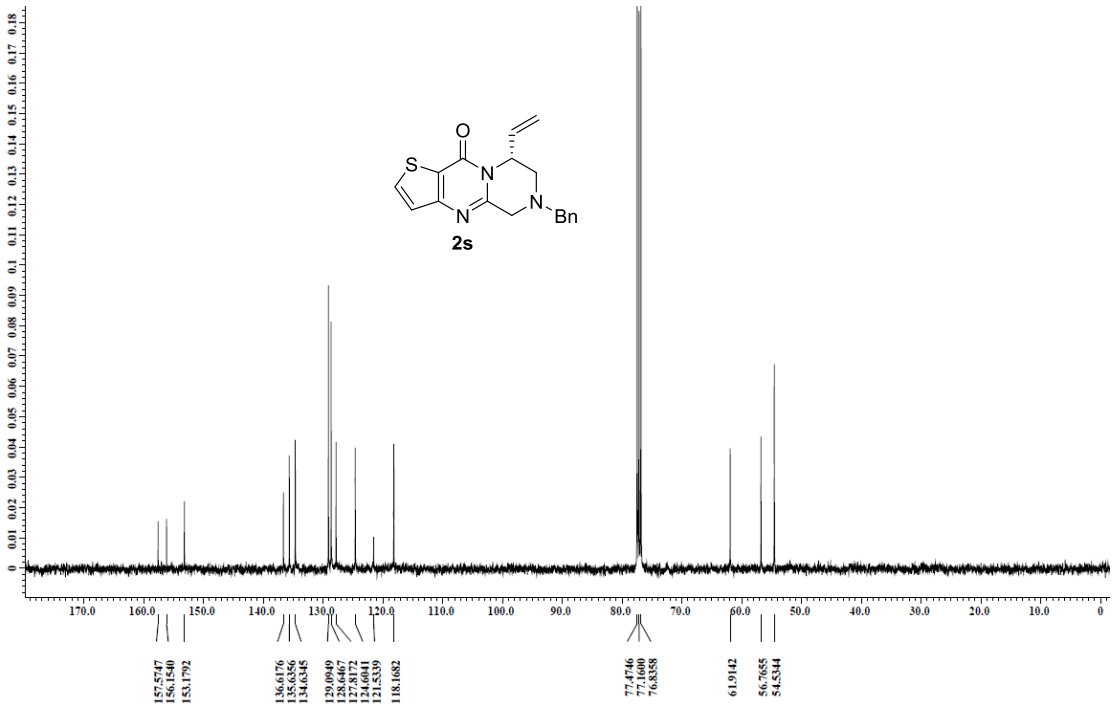
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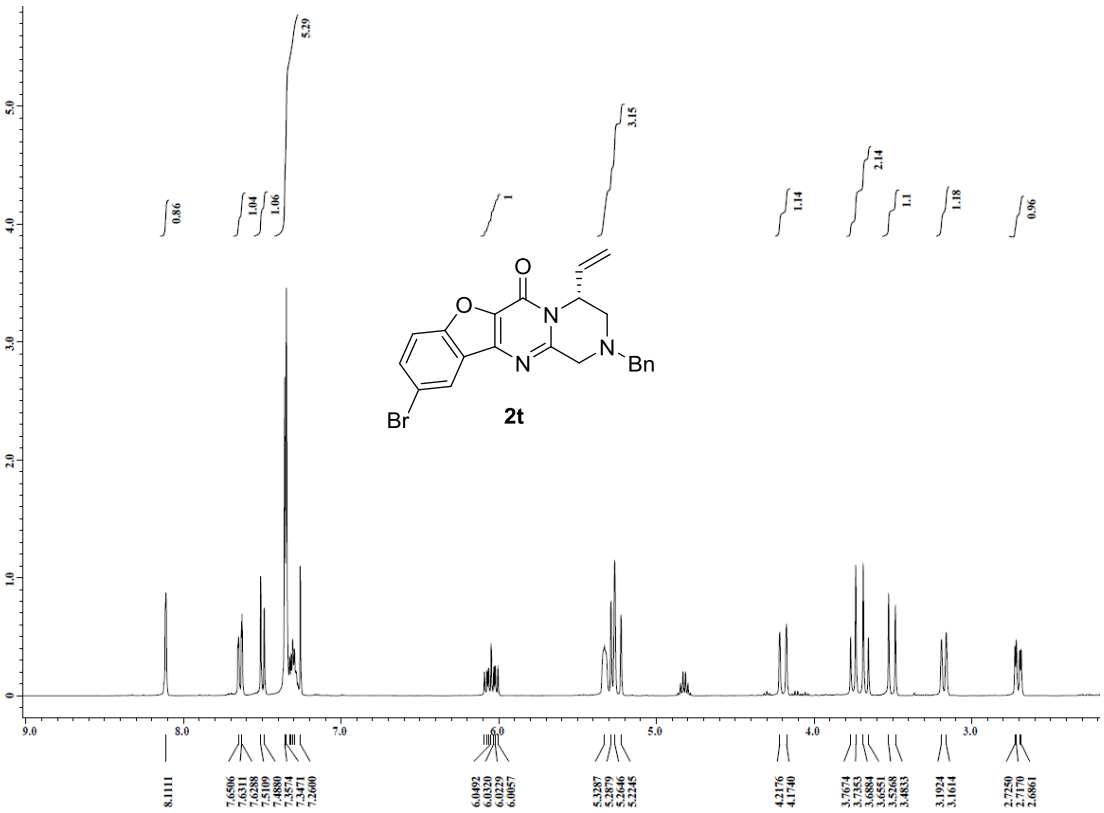
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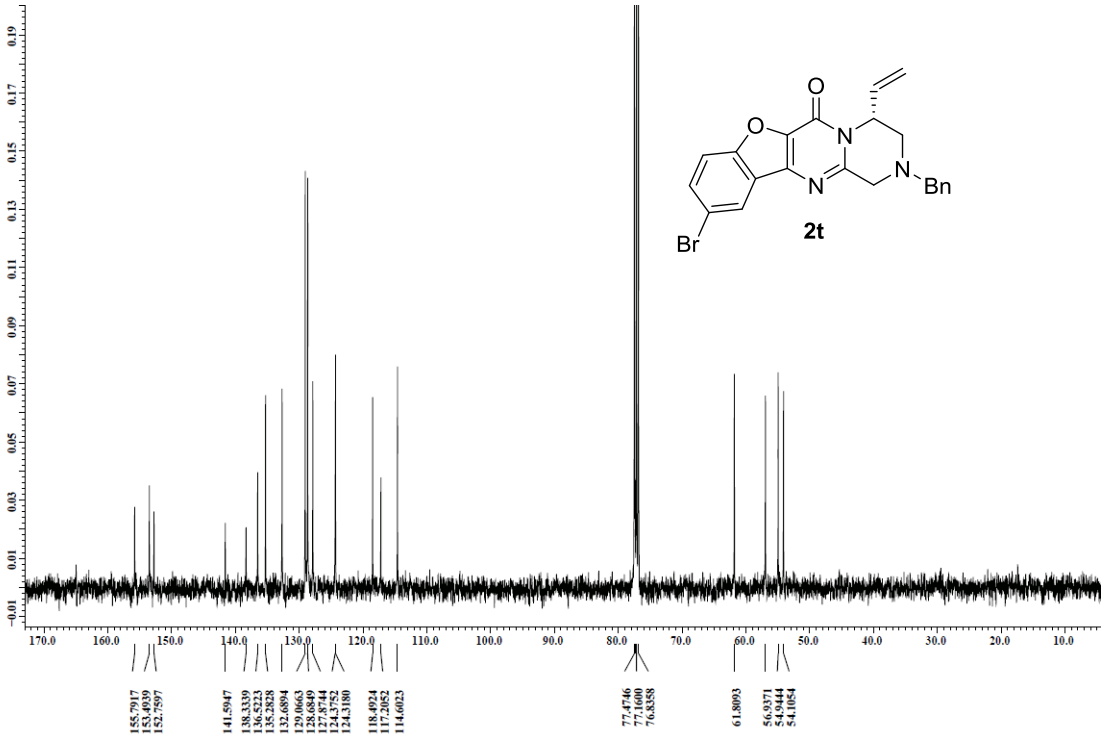
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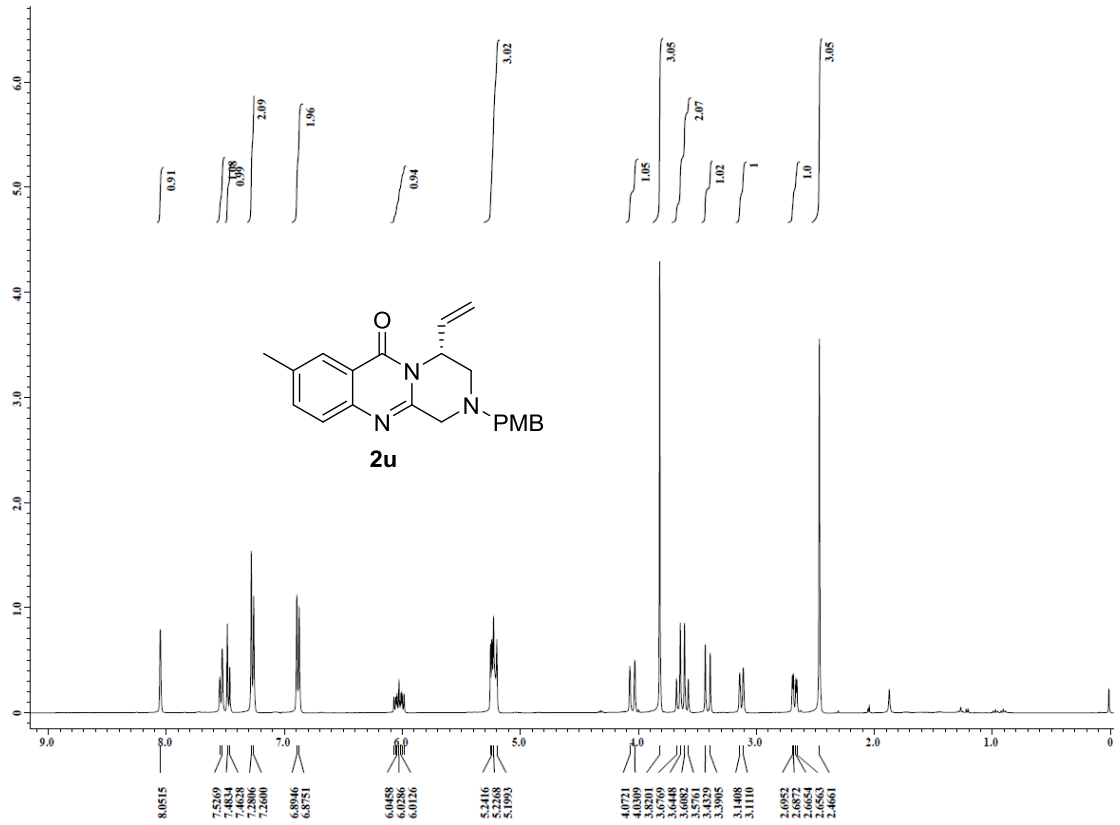

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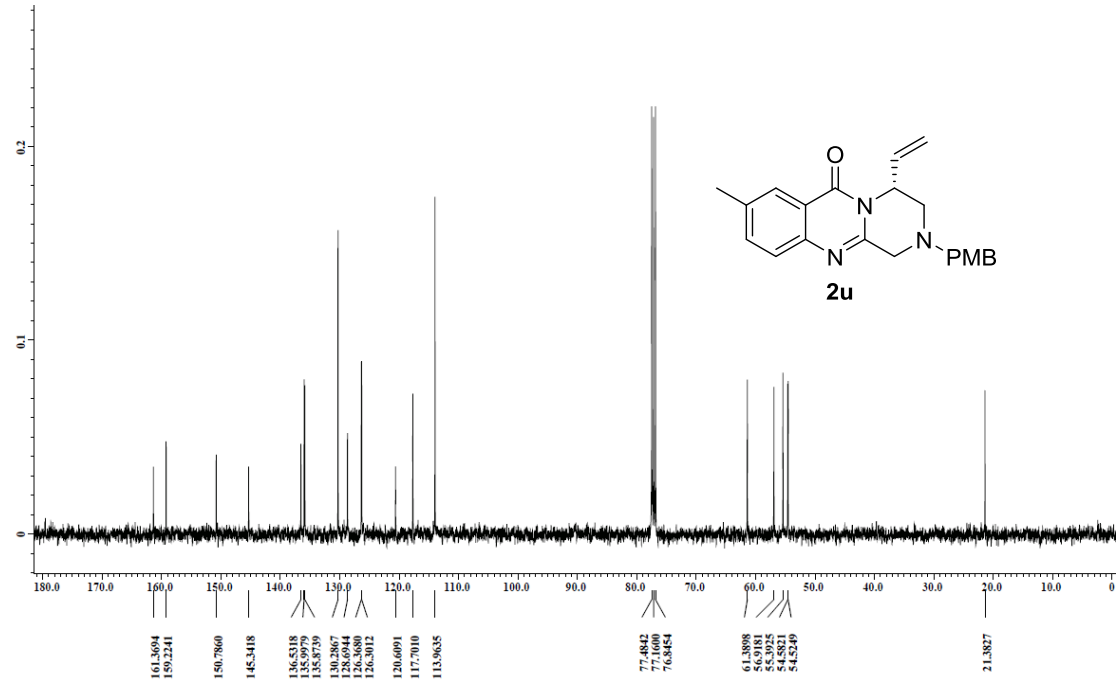

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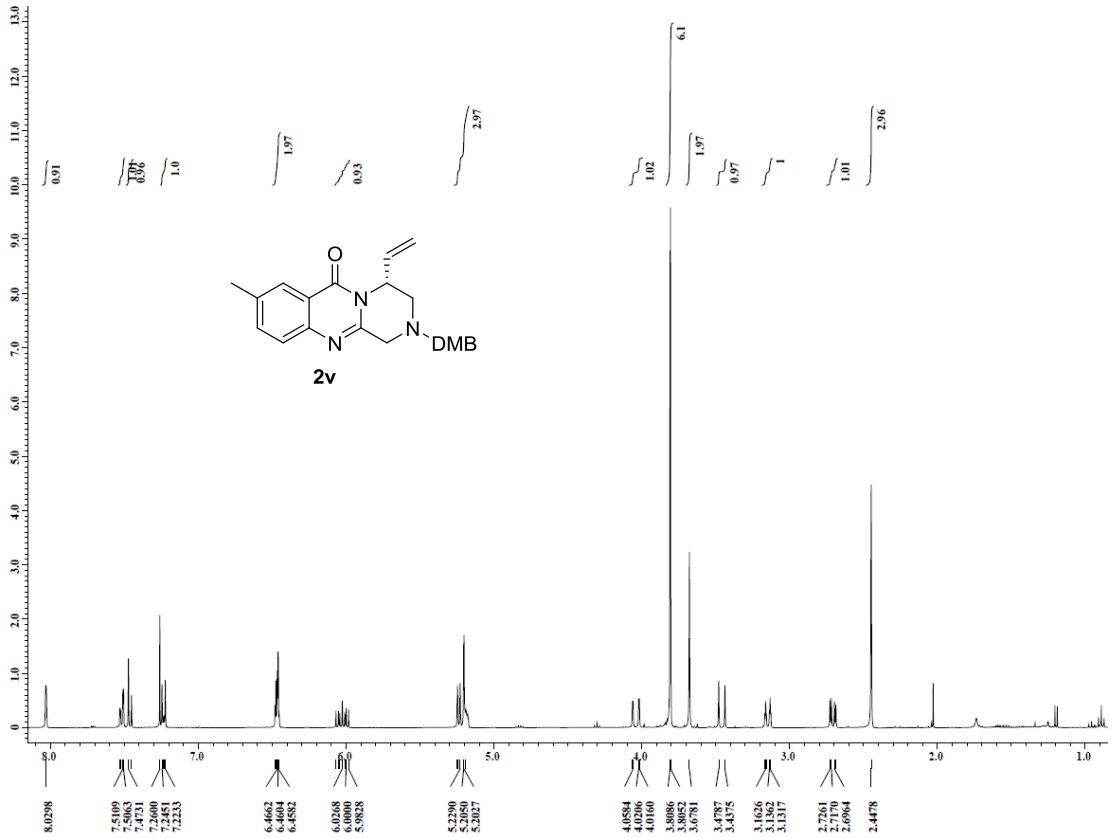

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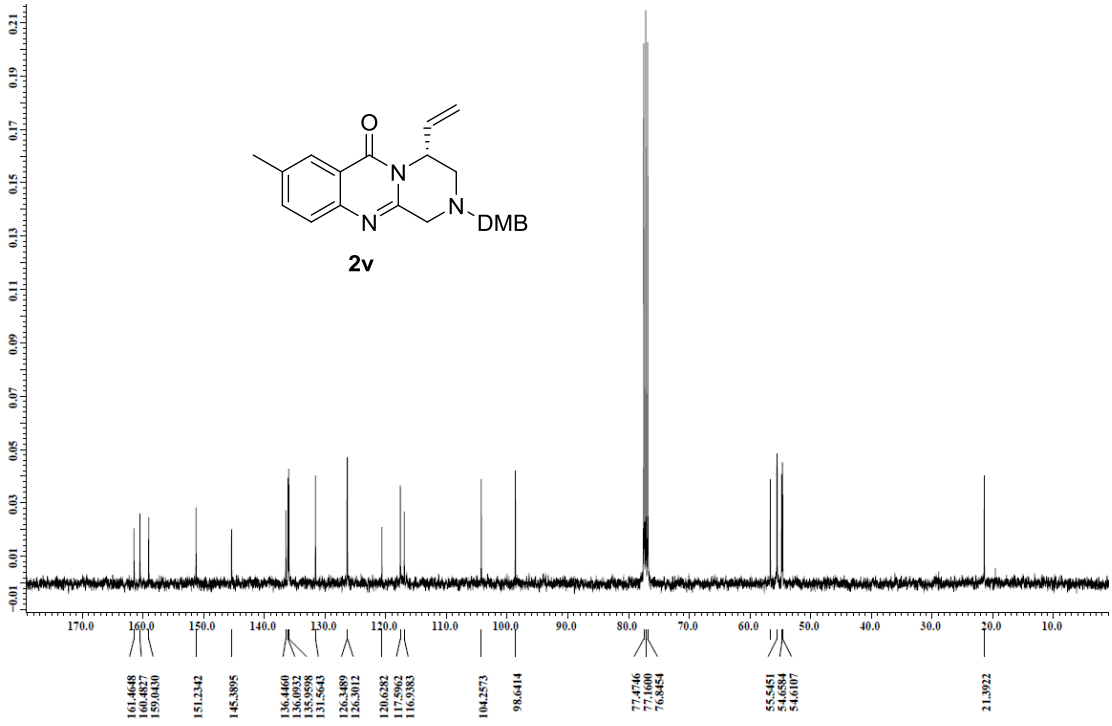

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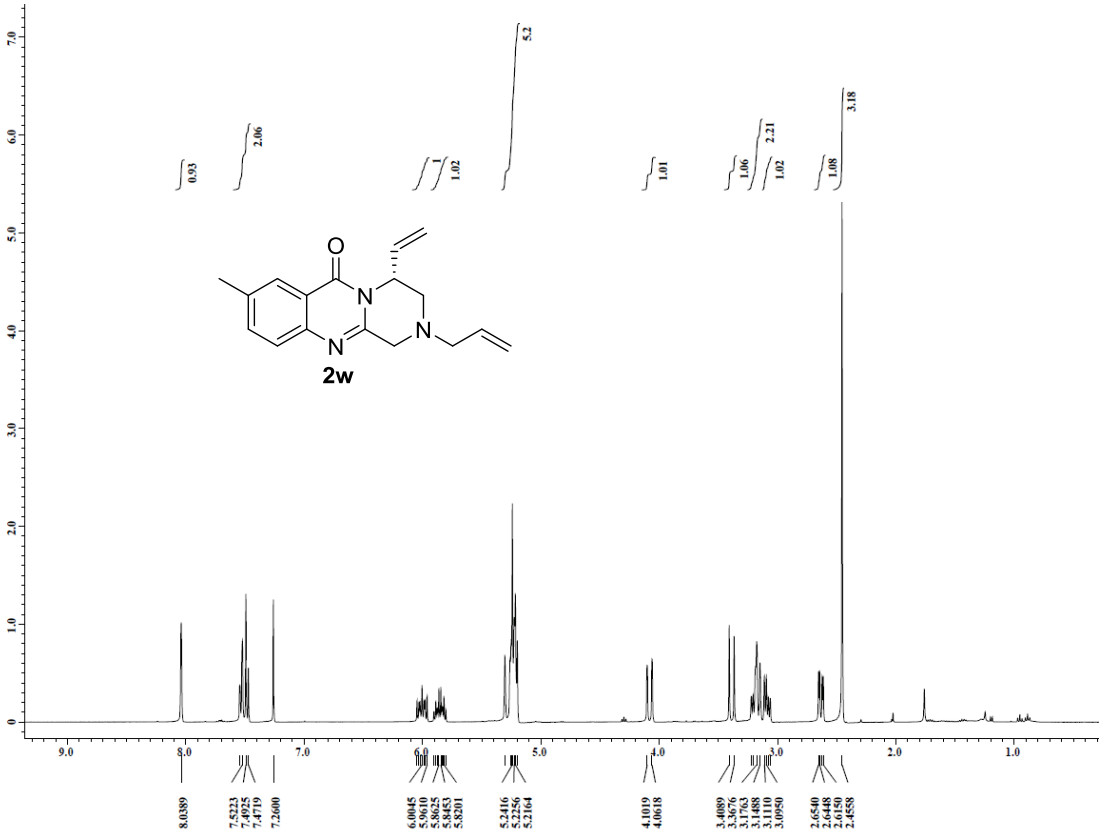
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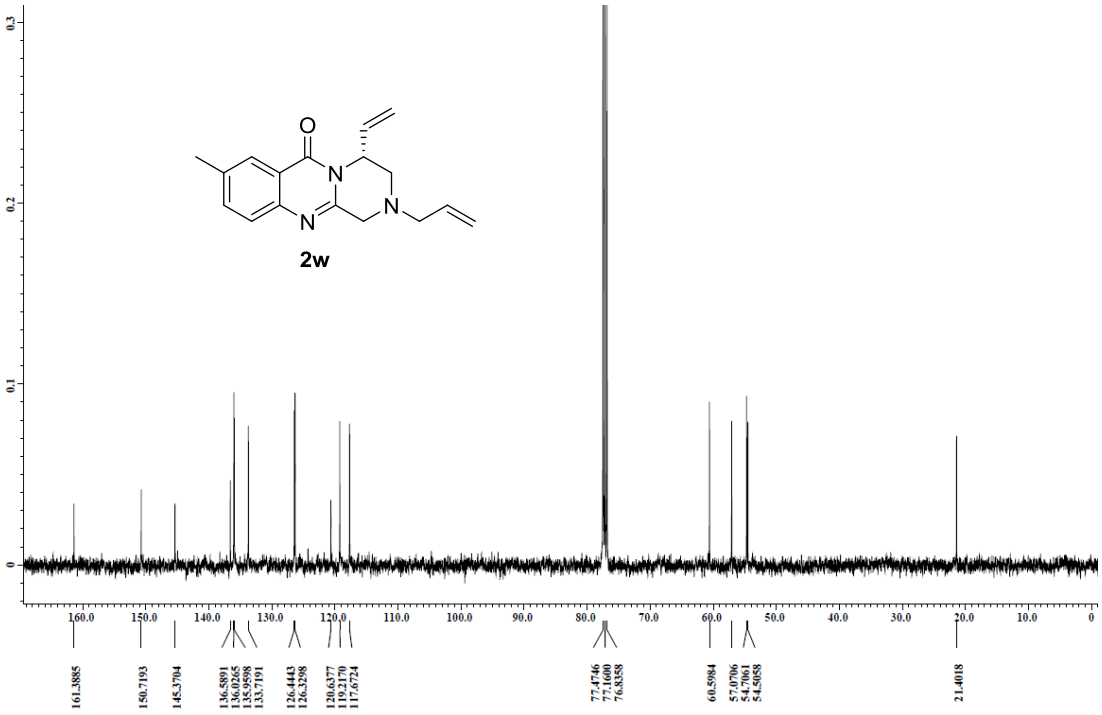
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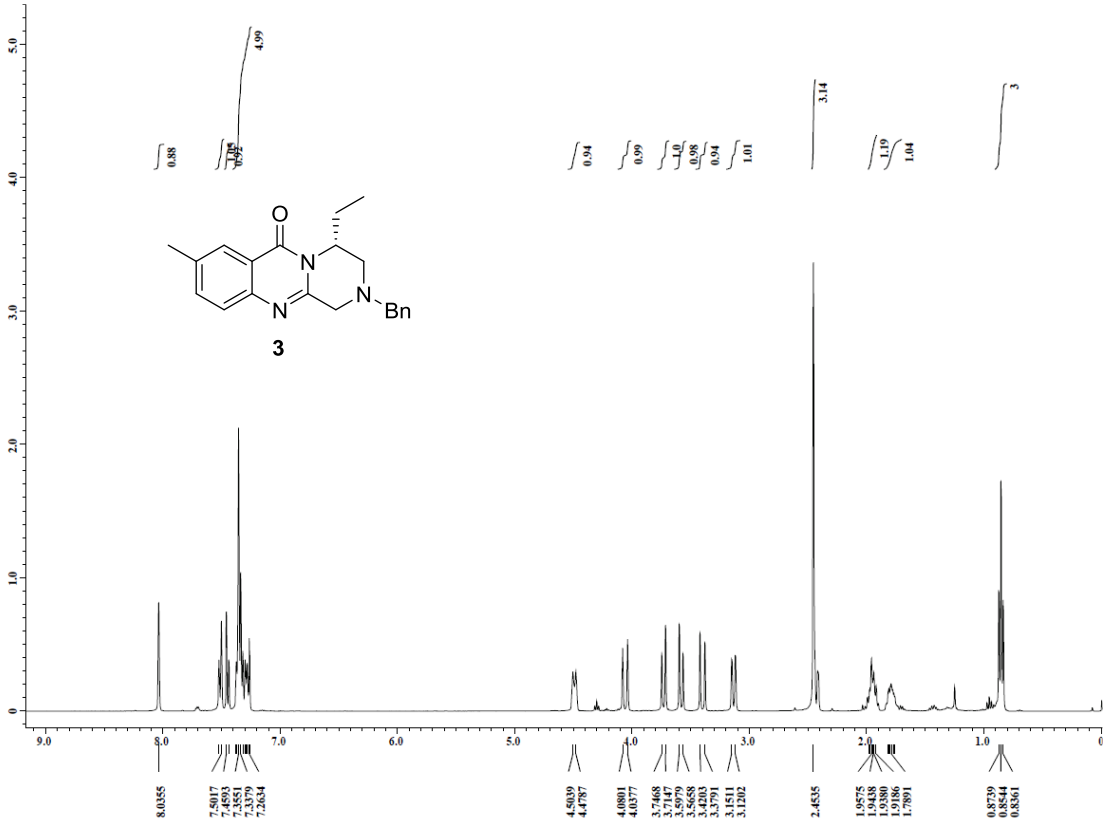
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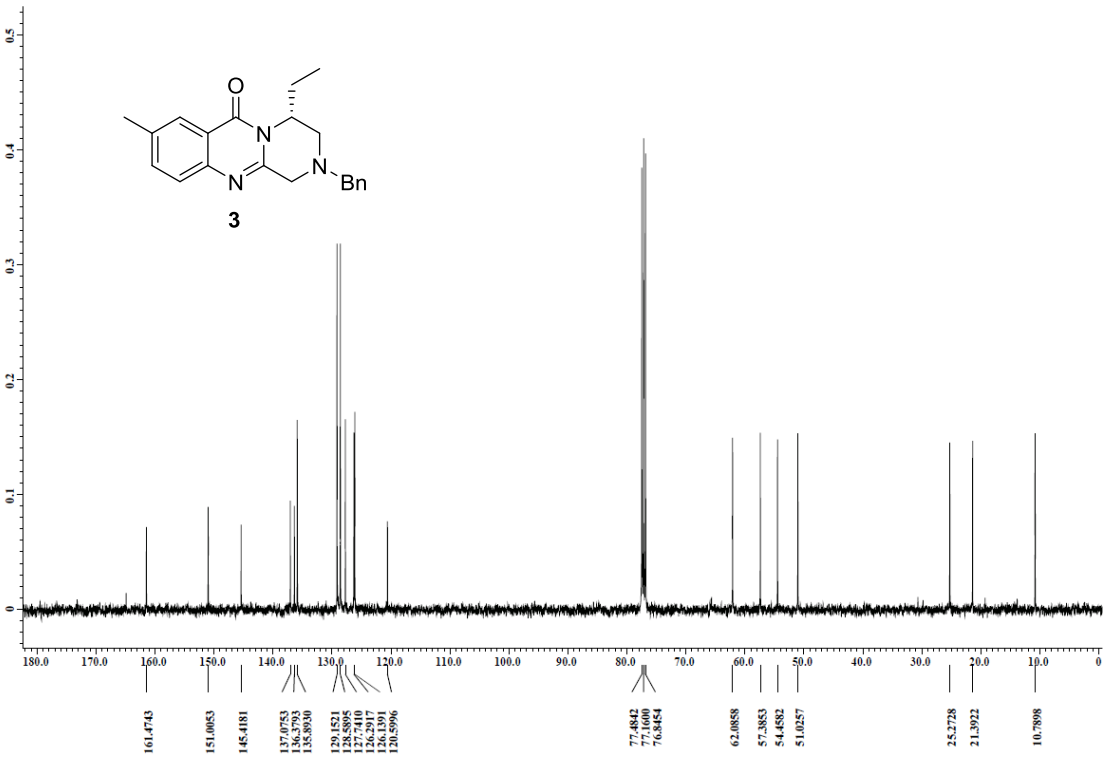
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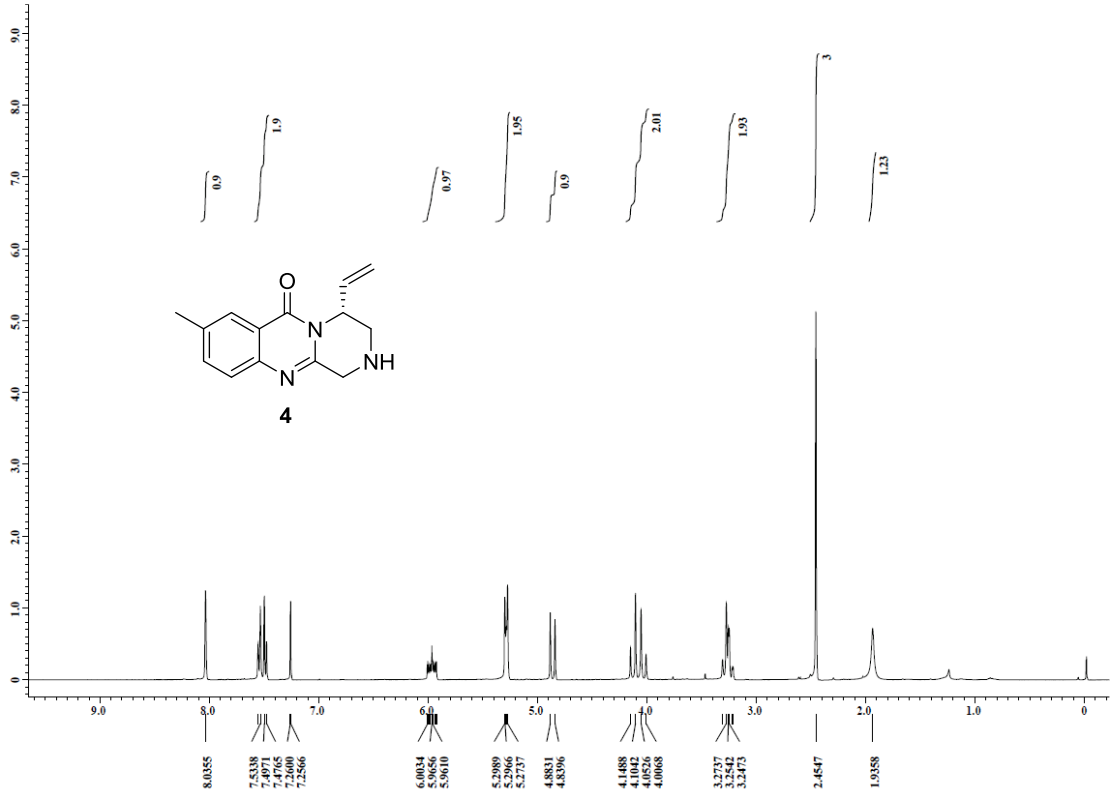
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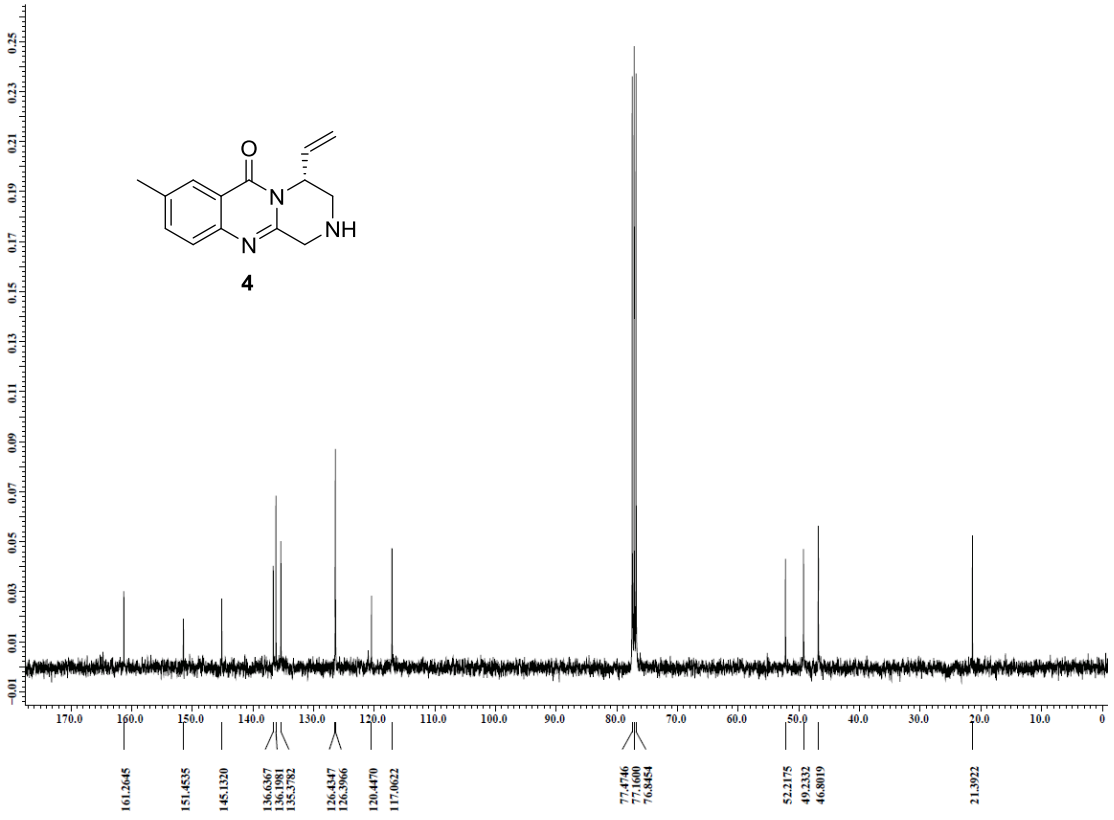
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